THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY

BY

(the late)

JOCELYN FIELD THORPE, Kt., C.B.E., D.Sc., F.R.S., F.I.C.

Emeritus Professor of Organic Chemistry in the University of London and in the Imperial College of Science and Technology. Past President of the Chemical Society and of the Institute of Chemistry

AND

M. A. WHITELEY, O.B.E., D.Sc., F.I.C.

Lately Assistant Professor of Organic Chemistry, Imperial College of Science and Technology

ASSISTED BY EMINENT CONTRIBUTORS

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FOREWORD

THE general scheme outlined in the preface to Volume I has been followed in the preparation of Volume II, although certain suggestions made by reviewers and others have been adopted. One or two reviewers of Volume I, for example, made the remark that too much space had been given to Organic Chemistry. This is, however, more apparent than real, for if the pages allotted to each of the chief branches of Chemistry be numbered, it will be found that, counting only the reading matter, more space has been allotted, in both Volumes I and II, to the Inorganic and Physical branches of Chemistry than to the Organic section. It is the space occupied by Organic formulæ which makes these articles so bulky and thus gives them the appearance of predominance. We have done our best to reduce this bulk and have been able to do so in many cases without detriment to the article involved. We hold the view that articles in a dictionary of this kind must be clearly and concisely written, and no modern article on a subject in Organic Chemistry can be constructed to comply with these conditions unless it is illustrated by elaborate formulæ.

Again, the comment has been made that the new edition of the Dictionary appears to be written on a fundamental basis and seems, therefore, to have little to do with "Applied Chemistry." It is interesting, in this connection, to note the difference in meaning which the word "Applied" has undergone since the first edition of the Dictionary was published. In those days the words "Applied Chemistry" meant the field in which the *chemical technician* worked, and it was necessary for such a worker to possess a wide knowledge of chemistry; he consulted the Dictionary in order to obtain information on subjects on which he was working at that moment. The Dictionary was made for such as he, and we aim at maintaining its value from this point of view. On the other hand, the passage of time has led to the general recognition that there are not two branches of Chemistry, "Pure" and "Applied," but only one kind, and that the "Applied" or "Industrial" side must be based on pure chemistry if it is to exist and prosper. We have therefore continued the plan adopted in Volume I and have inserted a number of monographs on fundamental matters, while, at the same time, retaining the articles on leading industries after bringing them up to date. In the matter of illustrations of technical plant we have avoided, and intend to avoid as far as may be possible, the reproduction of illustrations from the advertisement pages of the Chemical and Chemical Engineering Press. The apparatus illustrated in this way often deals with appliances made for a specific purpose, while it is the object of the Dictionary to be as general as possible. Nevertheless, we propose to draw freely from such illustrations when necessary, provided they are specific to the article in question. When special drawings are required they will be provided.

Again we have to thank all concerned for the ready help they have accorded us. Especially is this the case with the Printers, who took great pains and patience to follow our requirements in the matter of Organic formulæ. The success of their work is shown in the text and is self-evident. They are heartily to be congratulated on the completion of a difficult and onerous task.

We have also to thank those who have given us permission to reproduce figures and tables from periodicals controlled by them.

J. F. THORPE
M. A. WHITELEY

South Kensington,
June. 1938.

LIST OF CONTRIBUTORS

TO VOLUME II

NOEL L. ALLPORT, F.I.C., *The British Drug Houses, Ltd.* [CHEMICAL ANALYSIS :—*Drop Reactions (" Spot " Tests), Colorimetric Analysis.*]

H. R. AMBLER, Ph.D., F.I.C., *Chemist, Research Department, Woolwich.* [CHEMICAL ANALYSIS :—*Gas Analysis ; Gas Volumetric Methods of Analysis.*]

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G. F. BLOOMFIELD, Ph.D., D.I.C., A.I.C., *Research Chemist, The British Xylonite Co., Ltd.* [BRASSIDIC ACID ; BRASSYLIC ACID.]

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Dr. R. CHAPLIN, A.I.C., *Research Chemist.* [CARBON :—*Charcoal, Active.*]

WALTER CLARK, M.Sc., Ph.D.(Lond.), *Assistant to Director of Research, Research Laboratory, Eastman Kodak Co., Rochester, N.Y.* [CELLULOID PLASTICS :—*Photographic Film.*]

R. S. COLBORNE, B.Sc., A.R.C.S., D.I.C., A.I.C., *Manager, Synthetic Camphor Dept., British Xylonite Co., Ltd., Brantham Works, Nr. Manningtree, Essex.* [CAMPHOR, SYNTHETIC.]

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A. E. DUNSTAN, D.Sc., F.I.C., *Chief Chemist, Anglo-Iranian Oil Co., Ltd., Britannic House, London, E.C.*2. [BLAU GAS ; BUTANE AS A FUEL ; CELLOSOLVE.]

A. J. EWINS, D.Sc., *Director of Research, May and Baker, Ltd., Dagenham.* [CAFFEINE AND THE ALKALOIDS OF TEA, COFFEE, AND COCOA.]

E. H. FARMER, D.Sc., F.I.C., *Lecturer in Organic Chemistry, Imperial College of Science and Technology, London, S.W.7.* [BUTADIENES AND POLYOLEFINS (CONJUGATED); BUTADIENES AND POLYOLEFINS (NON CONJUGATED).]

E. A. FISHER, M.A., D.Sc., *Director of Research, The Research Association of British Flour Millers, St. Albans.* [CEREALS.—*Bran, Maize, Oats, Wheat.*]

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R. H. PURCELL, Ph.D., D.I.C., *Assistant Lecturer, Physical Chemistry, Imperial College of Science and Technology, London, S.W.7.* [BUFFER SOLUTIONS ; CHEMICAL AFFINITY.]

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ROSE SCOTT-MONCRIEFF (Mrs. O. M. MEARES), Ph.D., B.Sc., A.R.C.S., *late of the John Innes Horticultural Institution, S.W.19.* [CALLISTEPHIN ; CARAJURIN.]

H. SHANKSTER, F I C , *Senior Chemist, Department of the W. D. Chemist, Royal Arsenal, Woolwich, S E.18.* [BLASTING GELATINE, CENTRALITES, CHEDDITE; CHEESA STICKS]

Professor J L SIMONSEN, D.Sc, F.I.C, F R S, *University College of North Wales, Bangor.* [BORNEOL AND *iso*BORNEOL; BORNYL CHLORIDE AND *iso*BORNYL CHLORIDE; BORNYLENE, *apo*BORNYLENE; BUPLEUROL, CADINENE, CADINOL, CALAMENE; CALAMENOL, CALAMEON; CAMPHENE, CAMPHENILONE, CAMPHOR, Δ^3-CARENE; Δ^4 CARENE; CARONE; CARVENONE; CARVEOL, CARVOMENTHOL, CARVOMENTHONE, CARVONE; CARVOTANACETONE; CARYOPHELLENES, CEDRENE, CEDROL]

L. J. SPENCER, C B E, M A, Sc D, F.R S, *Editor of the Mineralogical Magazine. Formerly Keeper of Minerals in the British Museum.* [BLOEDITE, BLOMSTRANDINE; BLOODSTONE; BLUE IRON EARTH, BOEHMITE OR BOHMITE, BOG IRON ORE, BOLE, BORACITE; BORAX; BORNITE, BORONATROCALCITE, BOSTONITE; BOURNONITE; BRAGGITE; BRAUNITE; BRAZILITE, BROCHANTITE, BRÖGGERITE, BROMELLITE; BRUCITE; BULTFONTEINITE; BURRSTONE OR BUHRSTONE, BUSZITE, BUTTGENBACHITE; CALAMINE, CALAVERITE; CALCITE OR CALC SPAR, CANNIZZARITE, CARBON (GRAPHITE); CARBONITE; CARCLAZITE OR CARCLAZYTE, CARNALLITE, CARNOTITE, CASSITERITE OR TIN STONE, CATAPLEIITE; CELESTINE OR CELESTITE; CERARGYRITE OR HORNSILVER; CERITE; CERUSSITE; CHALCANTHITE; CHALCEDONY, CHALCOPYRITE; CHALCOSINE, CHALCOCITE, CHALCOSTIBITE OR WOLFSBERGITE, CHALK; CHALYBITE.

F S SPRING, D Sc, Ph D, *Lecturer in Chemistry, The University, Manchester* [BOSWELLINIC ACID]

FOSTER SPROXTON, B Sc (Lond), F I C, *Director, British Xylonite Co, Ltd, Brantham Works, Manningtree* [CELLULOID]

GEORGE STUBBS, C B E, F I C, *Formerly "The Deputy Government Chemist"* [BUTTER]

FRANCIS G H TATE, F I C, *Superintending Chemist, Government Laboratory, London* [BRAGA; BRANDY, CHARTREUSE]

A. L THOROGOOD, B Sc (Lond), *Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington* [CHEMICAL ANALYSIS:—*Analytical Applications of Spectroscopy*]

A. R TODD, B Sc, D Phil Nat (Frankfurt), D Phil.(Oxon), D Sc (Glasgow), *Assistant in the Department of Biochemistry, Lister Institute, Reader in Biochemistry in the University of London.* [CARDIAC GLYCOSIDES]

DAVID TRAILL, B Sc, Ph D, *I C I (Explosives Group), Ltd* [CELLULOSE PLASTICS · CELLULOSE ESTER PLASTICS, CELLULOSE ETHER PLASTICS

E E WALKER, D Sc (Lond.), D I C, A C G I [CATALIN.]

M A WHITELEY, O B E, D.Sc., F I C, *formerly Assistant Professor of Organic Chemistry, Imperial College of Science and Technology, London, S.W 7,* and W V. THORPE, M A, Ph D, *Reader in Chemical Physiology, University of Birmingham* [CARNINE, CARNITINE, CARNOSINE]

ABBREVIATIONS

OF THE TITLES OF JOURNALS, ETC.

(Reproduced by permission of the Bureau of Abstracts.)

A. I; *A.* II; *A.* III	British Chemical and Physiological Abstracts.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Acta Bot. Fennica	Acta Botanica Fennica.
Acta Physicochim. U.R.S.S.	Acta Physicochimica U.R.S.S.
Acta Phytochim.	Acta Phytochimica.
Acta Sci. Fennicæ	Acta Societatis Scientiarum Fennicæ.
Agric. Eng.	Agricultural Engineering.
Agric. Gaz. New South Wales	Agricultural Gazette of New South Wales.
Agric. J. Brit. Guiana	Agricultural Journal of British Guiana.
Agric. Live-stock India	Agriculture and Live-stock in India.
Agric. Res. Inst., Pusa, Rep. (Bull.)	Agricultural Research Institute, Pusa, Reports and Bulletins.
Allgem. Oel- Fett-Ztg.	Allgemeine Oel- und Fett-Zeitung.
Allgem. Z. Bierbrau.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Aluminium	Aluminium.
Amer. Chem. Abstr.	Chemical Abstracts. Published by the American Chemical Society.
Amer. Dyestuff Rep.	American Dyestuff Reporter.
Amer. Gas J.	American Gas Journal.
Amer. Ink Maker	American Ink Maker.
Amer. Inst. Min. Met. Eng. Publ.	American Institute of Mining and Metallurgical Engineers Publication.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Children	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health and the Nation's Health.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Amer. Paint J.	American Paint Journal.
Amer. Potato J.	American Potato Journal.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Española de Física y Química.
Anal. Inst. invest. cient. tecn.	Anales del Instituto de investigaciones científicas y tecnológicas.
Analyst	Analyst.
Anat. Rec.	Anatomical Record.
Angew. Bot.	Angewandte Botanik.
Angew. Chem.	Angewandte Chemie (changed from Z. angew. Chem. in 1932).
Anilinokras. Prom.	Anilinokrasotschnaja Promischlennosti.
Ann. Acad. Brasil. Sci.	Annals da Academia Brasileira de Sciencias.
Ann. Acad. Sci. Fennicæ	Annales Academiæ Scientiarum Fennicæ.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. agron.	Annales agronomique.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Annali Chim. Appl.	Annali di Chimica Applicata.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique et de Chimie Appliquée.
Ann. di Bot.	Annali di Botanica.
Ann. Falsif.	Annales des Falsifications.
Ann. Ferm.	Annales des Fermentations.
Ann. Inst. Anal. Phys. Chim.	Annales de l'Institut d'Analyse Physico-chimique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Mines Belg.	Annales des Mines de Belgique.

Ann. Off. nat. Comb. liq.	Annales de l'Office nationale des Combustibles liquides.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. Sect. Platine	Annales du Secteur Platine et des autres Métaux Précieux.
Ann. Sci.	Annals of Science.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Sci. Bruxelles	Annales de la Société Scientifique de Bruxelles.
Apoth.-Ztg.	Apotheker-Zeitung.
Arb. Biol. Reichanst. Land u. Forstwirts.	Arbeiten der Biologisches Reichanstalt fur Land- und Forstwirtschaft.
Arbeitsphysiol.	Arbeitsphysiologie.
Arch. Biol.	Archives de Biologie.
Arch. Eisenhüttenw.	Archiv. für das Eisenhüttenwesen.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie Pharmakologie.
Arch. Farm. sperim.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Gewerbepath. Gewerbehyg.	Archiv fur Gewerbepathologie und Gewerbehygiene.
Arch. Hyg. Bakt.	Archiv der Hygiene und Bakteriologie.
Arch. Int. Med.	Archives of Internal Medicine.
Arch. int. Physiol.	Archives internationales de Physiologie.
Arch. Ist. Biochim. Ital.	Archivio dello Istituto Biochimico Italiano.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Min. Soc. Sci. Varsovie	Archives de Minéralogie de la Société des Sciences de Varsovie (Archivum Mineralogiczne Towarzystwa Naukowego Warszawskiego).
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. Physiol.	Archives Néerlandaises de Physiologie de l'Homme et des Animaux.
Arch. Pflanzenbau	Archiv. für Pflanzenbau.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Protistenk.	Archiv für Protistenkunde.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arch. Tierernährung u Tierzucht	Archiv für Tierernährung und Tierzucht.
Arch. Wärmewirts.	Archiv für Wärmewirtschaft.
Arizona Agric. Exp. Sta. Bull.	Arizona Agricultural Experiment Station Bulletin.
Arkiv Kemi, Min., Geol.	Arkiv for Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysics Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Austral. J. Exp. Biol.	Australian Journal of Experimental Biology and Medicine.
B.	British Chemical Abstracts. B.—Applied Chemistry.
B P.	British Patent.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Ber. Ges. Kohlentech.	Berichte der Gesellschaft für Kohlentechnik.
Ber. Sächs. Akad. Wiss.	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Ber. Ukrain. Wiss. Forsch physikal. Chem.	Berichte des Ukrainischen Wissenschaftlichen Forschungsinstituts fur physikalische Chemie.
Berlin. klin. Woch.	Berliner klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt.
Bied. Zentr. (Tierernähr.)	Biedermann's Zentralblatt (*Tierernährung*).
Biochem. J.	Biochemical Journal
Biochem. Z.	Biochemische Zeitschrift.
Biochimia	Biochimia.
Bodenk. Pflanzenernähr.	Bodenkunde und Pflanzenernährung.
Bol. Acad. Nac. Ciencias, Cordoba	Boletín de la Academia Nacional des Ciencias, Cordoba.
Bol. Soc. Quím. Peru	Boletín de la Sociedad Química del Peru.
Boll. Chim. farm.	Bollettino Chimico-Farmaceutico.
Boll. Sez. Ital.	Bolletino della Sezione Italiana.
Boll. Soc. Geol. Ital.	Bollettino della Società Geologica Italiana.
Boll. Soc. Ital. Biol. sperim.	Bolletino della Societa Italiana di Biologia sperimentalla.
Boll. Soc. Med.-Chirurg.	Bollettino della Società Medico Chirurgica, Pavia.
Boll. Uff. Staz. Sperim. Ind. Essenze.	Bollettino Ufficiale della R. Stazione Sperimentale per l'Industria delle Essenze e dei Derivati dagli Agrumi in Reggio Calabria.

Boll. Uff. Staz. Sperim. Ind. Pelli.	R. Stazione Sperimentale per l'Industria delle Pelli e delle materie concianti, Bollettino Ufficiale.
Bot. Archiv	Botanisches Archiv.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Braunkohlenarchiv	Braunkohlenarchiv.
Brennstoff-Chem.	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. Dental J.	British Dental Journal.
Brit. Guiana Dept. Agric. Bull.	British Guiana Department of Agriculture Bulletin.
Brit. J. Exp. Path.	British Journal of Experimental Pathology.
Brit. J. Phot.	British Journal of Photography.
Brit. J. Phys. Med.	British Journal of Physical Medicine.
Brit. Med. J.	British Medical Journal.
Brit. Plastics	British Plastics and Moulded Products Trader.
Bul. Chim.	Buletinul Chimie.
Bul. Chim. Soc. Române	Buletinul de Chimie pura si aplicata al Societatii Române de Chimie.
Bul. Soc. Chim. România	Buletinul Societătii de Chimie din România.
Bul. Soc. Fiz. România	Buletinul Bilunar al Societătii de Fizică din România.
Bul. Soc. Române Stiin.	Buletinul Societatii Române de Stiinte.
Bull. Acad. Méd. Roumanie	Bulletin de l'Académie de Médecine de Roumanie.
Bull. Acad. Polonaise	Bulletin Internationale de l'Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Agra & Oudh	Bulletin of the Academy of Sciences of Agra and Oudh.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Agric. Chem. Soc. Japan	Bulletin of the Agricultural Chemical Society of Japan.
Bull. Amer. Ceram. Soc	Bulletin of the American Ceramic Society.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Biol. Méd. exp. U.R.S.S.	Bulletin de Biologie et Médecine expérimentale de l'U.R.S.S.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Dept. Agric. Kenya	Bulletin of the Department of Agriculture of Kenya.
Bull. Dept. Agric. South Africa	Bulletin of the Department of Agriculture of South Africa.
Bull. Entomol. Res.	Bulletin of Entomological Research.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Inst. Min. Met.	Bulletin of the Institution of Mining and Metallurgy.
Bull. Inst. Phys. Chem. Res. Japan.	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikagaku Kenkyujo Ihō).
Bull. Inst. Pin	Bulletin de l'Institut du Pin.
Bull. Johns Hopkins Hosp.	Bulletin of the Johns Hopkins Hospital.
Bull. Mat. Grasses	Bulletin des Matières Grasses.
Bull. Photogrammétrie	Bulletin de Photogrammétrie.
Bull. Rubber Growers' Assoc.	Bulletin of the Rubber Growers' Association.
Bull. School Mines and Met., Univ. Missouri.	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bull. Sericult. Japan	Bulletin of Sericulture and Silk Industry, Japan.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. Chim. Yougoslav.	Bulletin de la Société Chimique du Royaume de Yougoslavie.
Bull. Soc. d'Encour.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. Franç. Min.	Bulletin de la Société Française de Minéralogie.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie et de Cinématographie.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Sci. Hyg. aliment.	Bulletin de la Société Scientifique d'Hygiène alimentaire.
Bull. U.S. Geol. Survey	Bulletin of the U.S. Geological Survey.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.

Canad. Chem.	Canadian Chemistry and Process Industries.
Canad Chem. Met.	Canadian Chemistry and Metallurgy.
Canad Dairy & Ice Cream J.	Canadian Dairy and Ice Cream Journal
Canad. J. Res.	Canadian Journal of Research.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Cellulosechem.	Cellulosechemie.
Cement and Lime Manuf.	Cement and Lime Manufacture.
Cereal Chem.	Cereal Chemistry.
Chaleur et Ind.	Chaleur et Industrie.
Chem. Age	Chemical Age.
Chem App.	Chemische Apparatur.
Chem. Eng Min Rev.	Chemical Engineering and Mining Review.
Chem. Erde	Chemie der Erde.
Chem Fabr.	Die Chemische Fabrik.
Chem and Ind.	Chemistry and Industry.
Chem Ind	Chemische Industrie.
Chem Listy	Chemické Listy pro Védu a Prûmysl Organ de la "Ceská chemická *Spolecnost pro Veda a Prûmysl.*"
Chem Met Eng	Chemical and Metallurgical Engineering.
Chem. Soc Annual Rep.	Annual Reports on the Progress of Chemistry.
Chem. Obzor.	Chemický Obzor.
Chem. Social Agric.	Chemisation of Socialistic Agriculture (U.S S.R.).
Chem Trade J.	Chemical Trade Journal.
Chem. Weekblad	Chemisch Weekblad.
Chem Zentr.	Chemisches Zentralblatt.
Chem -Ztg.	Chemiker Zeitung
Cheshunt Agric. Exp. Sta. Ann Rep	Cheshunt Agricultural Experiment Station Annual Reports.
Chim e l'Ind.	La Chimica e l'Industria.
Chim et Ind	Chimie et Industrie.
Chinese Med J.	Chinese Medical Journal.
Chinese J. Physics	Chinese Journal of Physics.
Chinese J. Physiol	Chinese Journal of Physiology.
Coal Age	Coal Age
Coal Carbonisation	Coal Carbonisation
Coll. Czech. Chem Comm.	Collection of Czechoslovak Chemica Communications.
Coll Eng.	Colliery Engineering.
Coll. Guard	Colliery Guardian.
Collegium	Collegium.
Colorado Agric. Exp. Sta. Bull	Colorado Agricultural Experiment Station Bulletin.
Combustion	Combustion.
Compt rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt rend Acad. Agric. France	Comptes rendus hebdomadaires des Séances de l'Académie d'Agriculture de France.
Compt rend. Acad. Sci. U R.S S	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
Compt. rend Soc. Biol	Comptes rendus des Séances de la Société de Biologie.
Compt rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Contr Boyce Thompson Inst	Contributions from Boyce Thompson Institute.
Cornell Univ. Agric. Exp Sta Bull.	Cornell University Agricultural Experiment Station Bulletin.
Current Sci.	Current Science.
Cyprus Agric. J.	Cyprus Agricultural Journal.
Dairy Ind.	Dairy Industry.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Delaware Agric. Exp. Sta Bull.	Delaware Agricultural Experiment Station Bulletin.
Dept Chem. S. Australia, Bull	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Zuckerind	Die Deutsche Zuckerindustrie.
East Malling Res Sta., Ann Repts., etc.	East Malling Research Station, Annual Reports, etc.
Ecology	Ecology.
Econ Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Empire Cotton Growing Rep Exp. Sta.	Empire Cotton Growing Reports of the Experimental Station.

Empire Cotton Growing Rev.	Empire Cotton Growing Review.
Empire J. Exp. Agric.	Empire Journal of Experimental Agriculture.
Engineer	Engineer.
Engineering	Engineering.
Eng. and Min. J.	Engineering and Mining Journal.
Enzymologia	Enzymologia.
Ergebn. Physiol.	Ergebnisse der Physiologie.
Ernährung	Die Ernährung.
Ernähr. Pflanze	Ernährung der Pflanze.
F.P.	French Patent.
Facts about Sugar	Facts about Sugar.
Farbe u. Lack	Farbe und Lack.
Farben-Chem.	Farben-Chemiker.
Farben-Ztg.	Farben-Zeitung.
Farve og Lak	Farve og Lak.
Fermentforsch.	Fermentforschung.
Fert. Feeding Stuffs J.	Fertiliser, Feeding Stuffs and Farm Supplies Journal.
Fette u. Seifen	Fette und Seifen.
Feuerfest	Feuerfest.
Feuerungstech.	Feuerungstechnik.
Finska Kem. Medd.	Finska Kemistsamfundets Meddelanden (Suomen Kemistiseuran Tiedonantoja).
Flora	Flora.
Florida Agric. Exp. Sta. Bull.	*Florida Agricultural Experiment Station Bulletin.*
Food	Food.
Food Manuf.	Food Manufacture.
Food Res.	Food Research.
Forstarchiv	Forstarchiv.
Foundry Trade J.	Foundry Trade Journal.
Fruit Prod. J.	Fruit Products Journal.
Fuel	Fuel in Science and Practice.
Fuel Econ.	Fuel Economist.
Fuel Econ. Rev.	Fuel Economy Review.
G.P.	German Patent.
Gas Ind.	Gas Industry.
Gas J.	Gas Journal.
Gas Times	Gas Times.
Gas- u. Wasserfach	Gas- und Wasserfach.
Gas World	Gas World.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Georgia Agric. Exp. Sta. Bull.	Georgia Agricultural Experiment Station Bulletin.
Ges. Abh. Kennt. Kohle	Gesammelte Abhandlungen der Kenntnis der Kohle.
Glass Ind.	Glass Industry.
Glasshütte	Die Glasshütte.
Glückauf	Glückauf.
Gummi-Ztg.	Gummi-Zeitung.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Helv. Chim. Acta	Helvetica Chimica Acta.
Hilgardia	Hilgardia.
Imp. Bur. Soil Sci. Tech. Comm.	Imperial Bureau of Soil Science, Technical Communications.
Indian J. Agric. Sci.	Indian Journal of Agricultural Science.
Indian J. Med. Res.	Indian Journal of Medical Research.
Indian J. Physics	Indian Journal of Physics.
Indian J. Vet. Sci.	Indian Journal of Veterinary Science.
Indian Lac Res. Inst. Bull.	Indian Lac Research Institute Bulletin.
India-rubber J.	India-rubber Journal.
Ind. Chem.	Industrial Chemist.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. [Anal.]	Industrial and Engineering Chemistry, Analytical Edition.
Int. Rev. Agric.	International Review of Agriculture.
Int. Sugar J.	International Sugar Journal.
Iron Age	Iron Age.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
J.C.S.	Journal of the Chemical Society.

Jahrb. geol. Reichsanst	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot	*Jahrbuch fur wissenschaftliche Botanik.*
Japan. J. Med. Sci.	Japanese Journal of Medical Sciences.
Japan. J. Physics	Japanese Journal of Physics.
Japan Nickel Rev.	*Japan Nickel Review.*
J. Agric. Chem. Soc Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Ceram. Soc	Journal of the American Ceramic Society.
J. Amer. Chem. Soc	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc	Journal of the American Medical Association
J. Amer. Pharm. Assoc	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron	Journal of the American Society of Agronomy
J. Amer. Soc Mech. Eng	Journal of the American Society of Mechanical Engineers.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association
J. Appl. Chem. Russia	Journal of Applied Chemistry, Russia.
J. Appl. Physics	Journal of Applied Physics (formerly Physics).
J. Assoc. Off. Agric. Chem	Journal of the Association of Official Agricultural Chemists.
J. Austral. Inst. Agric Sci.	Journal of the Australian Institute of Agricultural Science.
J. Bact	Journal of Bacteriology
J. Biochem. Japan	*Journal of Biochemistry, Japan*
J. Biol. Chem.	Journal of Biological Chemistry.
J. Brit. Dairy Farmers' Assoc	Journal of the British Dairy Farmers' Association.
J. Brit Wood Pres Assoc	Journal of the British Wood Preserving Association.
J. Canad Min Inst	Journal of the Canadian Mining Institute.
J. Cancer Res Comm Sydney.	Journal of the Cancer Research Committee of the University of Sydney.
J. Cell. Comp Physiol	Journal of Cellular and Comparative Physiology.
J Cellulose Inst. Tokyo	*Cellulose Industry, Journal of the Cellulose Institute, Tokyo.*
J Chem. Educ.	Journal of Chemical Education
J Chem Eng. China	Journal of Chemical Engineering, China.
J Chem. Ind. Russ	Journal of Chemical Industry, Russia.
J Chem Met. Soc S Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa
J Chem. Physics	Journal of Chemical Physics.
J. Chem. Soc Japan	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi)
J Chim phys.	Journal de Chimie physique.
J Chinese Chem Soc	Journal of the Chinese Chemical Society.
J Coll. Agric Hokkaido	Journal of the College of Agriculture, Hokkaido Imperial University, Japan
J Coll Agric. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo, Japan
J Coll Eng. Tokyo	Journal of the College of Engineering, Imperial University of Tokyo.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Counc. Sci. Ind. Res. Australia.	Journal of the Council of Scientific and Industrial Research of Australia
J Dairy Res.	Journal of Dairy Research.
J. Dairy Sci	*Journal of Dairy Science.*
J. Dept. Agric. I.F.S.	*Journal of the Department of Agriculture of the Irish Free State.*
J. Dept. Agric. Kyushu	Journal of the Department of Agriculture, Kyushu Imperial *University.*
J. Dept. Agric. S. Australia	Journal of the Department of Agriculture, South Australia.
J. Dept. Agric. Victoria.	Journal of the Department of Agriculture, Victoria.
J. Dept Agric. W. Australia	Journal of the Department of Agriculture, Western Australia.
J Ecology	Journal of Ecology.
J. Econ. Entomol.	Journal of Economic Entomology.
J. Egypt. Med. Assoc.	Journal of the Egyptian Medical Association.
J. Electrodep. Tech. Soc.	*Journal of the Electrodepositors Technical Society.*
J. Exp. Biol	Journal of Experimental Biology.
J Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.

J. Fuel Soc. Japan . . .	Journal of the Fuel Society of Japan.
J. Gen. Chem. Russ. . .	Journal of General Chemistry, Russia (formerly J. Russ. Phys. Chem. Soc.).
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo . . .	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Indian Chem. Soc. . .	Journal of the Indian Chemical Society.
J. Indian Inst. Sci. . . .	Journal of the Indian Institute of Science.
J. Ind. Hyg.	Journal of Industrial Hygiene and Toxicology.
J. Infect. Dis.	Journal of Infectious Diseases.
J. Inst. Brew.	Journal of the Institute of Brewing.
J. Inst. Electr. Eng. . . .	Journal of the Institution of Electrical Engineers.
J. Inst. Fuel.	Journal of the Institute of Fuel.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petroleum Tech. .	Journal of the Institution of Petroleum Technologists.
J. Inst. Sewage Purif. . .	Journal of the Institute of Sewage Purification.
J. Iron and Steel Inst. . .	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc. . .	Journal of the Japanese Ceramic Association.
J. Landw.	Journal für Landwirtschaft.
J. Marine Biol. Assoc. . .	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Min. Agric. N. Ireland .	Journal of the Ministry of Agriculture of Northern Ireland.
J. New England Water Works Assoc.	Journal of the New England Water Works Association.
J. Nutrition	Journal of Nutrition.
J. Oil Col. Chem. Assoc. .	Journal of the Oil and Colour Chemists' Association.
J. Opt. Soc. Amer. . . .	Journal of the Optical Society of America.
J. Org. Chem.	Journal of Organic Chemistry.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim. . . .	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther. . .	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan . .	Journal of the Pharmaceutical Society of Japan. (Yakugakuzasshi.)
J. Physical Chem. . . .	Journal of Physical Chemistry.
J. Phys. Chem. Russ. . .	Shurnal Fizitscheskoi Chimii.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén. . .	Journal de Physiologie et de Pathologie générale.
J. Phys. Radium . . .	Journal de Physique et le Radium.
J. Pomology	Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Austral. Chem. Inst.	Journal and Proceedings of the Australian Chemical Institute.
J. Proc. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.
J. Res. Nat. Bur. Stand. .	Journal of Research of the National Bureau of Standards.
J. Roy. Agric. Soc. . . .	Journal of the Royal Agricultural Society.
J. Roy. Hort. Soc. . . .	Journal of the Royal Horticultural Society.
J. Roy. Microscop. Soc. .	Journal of the Royal Microscopical Society.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Roy. Tech. Coll. . . .	Journal of the Royal Technical College (Glasgow).
J. Rubber Res.	Journal of Rubber Research.
J. Rubber Res. Inst. Malaya	Journal of the Rubber Research Institute of Malaya.
J. Sci. Hiroshima Univ. .	Journal of Science of the Hiroshima University.
J. Sci. Instr.	Journal of Scientific Instruments.
J. Sci. Tech. India . . .	Journal of Science and Technology, India.
J. Scot. Met. Soc. . . .	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan .	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Dyers and Col. . .	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech. . . .	Journal of the Society of Glass Technology.
J. Soc. Leather Trades' Chem.	Journal of the International Society of Leather Trades' Chemists.
J. S. African Chem. Inst. .	Journal of the South African Chemical Institute.
J. South-East. Agric. Coll. .	Journal of the South-Eastern Agricultural College, Wye, Kent.
J. State Med.	Journal of State Medicine.
J. Text. Inst.	Journal of the Textile Institute.
J. Univ. Bombay . . .	Journal of the University of Bombay.

J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
Kali	Kali.
Kautschuk	Kautschuk.
K. Svenska Vet. Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kentucky Agric. Exp. Stat. Bull.	Kentucky Agricultural Experimental Station, Bulletin.
Keram. Rundsch.	Keramisch Rundschau.
Kolloid Beih.	Kolloid Beihefte.
Kolloid Shurn	Kolloidni Shurnal.
Kolloid-Z	Kolloid-Zeitschrift.
Kunststoffe	Kunststoffe.
Lait	Le Lait.
Lancet	The Lancet
Landw Jahrb	Landwirtschaftliche Jahrbucher
Landw. Versuchs Stat.	Die landwirtschaftlichen Versuchs Stationen.
London Shellac Res. Bur., Tech Paper	London Shellac Research Bureau, Technical Paper.
Louisiana Planter	Louisiana Planter
Malay. Agric J.	Malayan Agricultural Journal.
Mass Agric. Exp Sta. Bull	Massachusetts Agricultural Experiment Station Bulletin.
Materie Plast	Materie Plastiche.
Medd. K. Vetenskapsakad. Nobel Inst	Meddelanden från Kongl-Vetenskapsakademiens Nobel Institut.
Med. Dośwad.	Medycyna Doświadczalna i Społeczna.
Mem. Accad. Lincei	Memorie della Reale Accademia Nazionale dei Lincei.
Mem. Accad Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem Coll Agric Kyoto	Memoirs of the College of Agriculture, Kyoto Imperial University.
Mem Coll Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Dept Agric. India	Memoirs of the Department of Agriculture in India
Mem. Inst. Chem Ukrain Acad Sci	Memoirs of the Institute of Chemistry, Ukrainian Academy of Sciences
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém Poudres	*Mémorial des Poudres.*
Mém Soc Ing Civ France	Mémoires et Compte rendu des Travaux de la Société des Ingénieurs Civils de France.
Metal Ind.	Metal Industry.
Metal Progr	Metal Progress.
Metall u. Erz	Metall und Erz.
Metallges. Rev.	Metallgesellschaft Periodic Review.
Metallurgia	Metallurgia.
Met. & Alloys	Metals and Alloys.
Metals Tech	Metals Technology.
Metrop. Water Bd Rep.	Metropolitan Water Board Reports.
Mich. Agric. Exp. Sta. Bull.	Michigan Agricultural Experiment Station Bulletin.
Mikrochem.	Mikrochemie.
Milch Forsch.	Milchwirtschaftliches Forschungen.
Milch Zentr.	Milchwirtschaftliches Zentralblatt.
Milk Ind.	Milk Industry.
Milk Plant Month.	Milk Plant Monthly.
Min Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. & Met.	Mining and Metallurgy.
Missouri Agric. Exp. Sta. Res. Bull.	Missouri Agricultural Experiment Station Research Bulletin.
Mitt. Kohlenforschungsinst. Prag	Mitteilungen des Kohlenforschungsinstituts in Prag.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und Hygiene.
Mitt. Materialprüf.	Mitteilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt med Ges Tokyo	Mitteilungen der medizinischen Gesellschaft zu Tokyo.
Mitt Path. Inst. K. Univ. Japan	Mitteilungen aus dem pathologischen Institut der Kaiserlichen Universitat zu Sendai, Japan
Mitt. Textilforsch. Krefeld	Mitteilungen der Textilforschungsanstalt Krefeld e.V.
Monatsh	Monatshefte fur Chemie und verwandte Teile anderer Wissenschaften.

Montana Agric. Exp. Sta. Bull.	Montana Agricultural Experiment Station Bulletin.
Month. J. Inst. Metals	Monthly Journal of the Institute of Metals.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Month. Rep. Dept. Agric. N. Ireland.	Monthly Reports of the Department of Agriculture of Northern Ireland.
Mühlenlab.	Das Mühlenlaboratorium.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nat. Butter & Cheese J.	National Butter and Cheese Journal.
Nat. Paint Var. Assoc. Circ.	National Paint, Varnish, and Lacquer Association, Inc., Circular.
Nature	Nature.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
Naturwiss.	Die Naturwissenschaften.
New Hamps. Agric. Exp. Sta. Bull.	New Hampshire Agricultural Experiment Station Bulletin.
New Jersey Agric. Exp. Sta. Bull.	New Jersey Agricultural Experiment Station Bulletin.
New Phytol.	New Phytologist.
New York Agr. Expt. Sta. Bull.	New York State Agricultural Experiment Station Bulletins.
New York (Geneva) Agric. Exp. Sta. Bull.	New York (Geneva) Agricultural Experiment Station Bulletin.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nutr. Abs.	Nutrition Abstracts and Reviews.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Oel u. Kohle	Oel und Kohle.
Off. Digest	Official Digest of the Federation of Paint and Varnish Production Clubs.
Ohio Agric. Exp. Sta. Bull.	Ohio Agricultural Experiment Station Bulletin.
Oil and Gas J.	Oil and Gas Journal.
Oil and Soap	Oil and Soap.
Oklahoma Agric. Exp. Sta. Bull.	Oklahoma Agricultural Experiment Station Bulletin.
Österr. Chem.-Ztg.	Österreichische Chemiker-Zeitung.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Pacific Pulp and Paper Ind.	Pacific Pulp and Paper Industry.
Paint Manuf.	Paint Manufacture.
Paint, Oil, and Chem. Rev.	Paint, Oil, and Chemical Review.
Paint Tech.	Paint Technology.
Paint and Var. Prod. Man.	Paint and Varnish Production Manager.
Paper	Paper.
Paper Ind.	Paper Industry.
Paper-Maker	Paper-Maker and British Paper Trade Journal.
Paper Trade J.	Paper Trade Journal.
Papier-Fabr.	Papier-Fabrikant.
Pedology	Pedology.
Peint., Pig., Ver.	Peinture, Pigment, Vernis.
Perf. & Essent. Oil Rec.	Perfumery and Essential Oil Record.
Petroleum	Petroleum (German).
Pflüger's Archiv	Archiv für die gesamte Physiologie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Ztg.	Pharmazeutische Zeitung.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Philippine Agric.	Philippine Agriculturist.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Physica	Physica.
Physical Rev.	Physical Review.
Physics	Physics (now Journal of Applied Physics).

Physikal. Z.	Physikalische Zeitschrift.
Physikal. Z. Sowjetunion	Physikalische Zeitschrift der Sovietunion.
Phytopath.	Phytopathology.
Phytopath. Z.	Phytopathologische Zeitschrift.
Plant Physiol.	Plant Physiology.
Planta (Z. wiss Biol)	Planta (Zeitschrift fur wissenschaftliche Biologie).
Plast. Massi	Plastitschekie Massi.
Poultry Sci.	Poultry Science.
Proc. Acad. Sci Agra and Oudh	Proceedings of the Academy of Sciences of the United Provinces of Agra and Oudh, India.
Proc. Amer. Acad. Arts Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Amer. Gas Assoc	Proceedings of the American Gas Association.
Proc. Amer. Phil. Soc	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol Soc.	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Test Mat.	Proceedings of the American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil Soc.	Proceedings of the University of Durham Philosophical Society.
Proc. Eng. Soc. W. Pa.	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy (Tokyo)
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Sciences.
Proc. Inst. Civ Eng	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. Internat. Cong. Soil Sci.	Proceedings of the International Congress of Soil Science.
Proc. Internat Soc. Soil Sci.	Proceedings of the International Society of Soil Science.
Proc. K. Akad. Wetensch Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Leningrad Dept. Inst. Fert.	Proceedings of the Leningrad Departmental Institute of Fertilisers.
Proc. Muslim Assoc.	Proceedings of the Muslim Association for the Advancement of Science.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotian Inst. Sci	Proceedings of the Nova Scotian Institute of Science.
Proc. Phil Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy Inst	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc Med	Proceedings of the Royal Society of Medicine.
Proc. Roy Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania	Proceedings of the Royal Society of Tasmania.
Proc. Sci. Assoc, Vizianagram.	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Exp Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. S. Wales Inst. Eng.	Proceedings of the South Wales Institute of Engineers.
Proc. Tech. Sect. Paper Makers' Assoc.	Proceedings of the Technical Section of the Paper Makers' Association of Great Britain and Ireland.
Proc. U.S. Nat. Mus.	Proceedings of the United States National Museum.
Protoplasma	Protoplasma.
Przemysl Chem.	Przemysl Chemiczny.
Publ. Fac. Sci. Univ. Masaryk.	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Přírodovědeckou Facoultou Masarykovy University).
Pulp and Paper Mag. Canada	Pulp and Paper Magazine of Canada.
Quart J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Quart J. Geol. Soc	Quarterly Journal of the Geological Society.
Quart. J Med.	Quarterly Journal of Medicine.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Queensland J. Agric.	Queensland Journal of Agriculture.
Rayon Text. Month.	Rayon Textile Monthly.
Rec. Australian Mus.	Records of the Australian Museum.
Rec. trav. bot. Néerland.	Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.

Refiner	Refiner and Natural Gasoline Manufacturer.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rensselaer Polyt. Inst. Bull.	Rensselaer Polytechnic Institute Bulletin.
Rep. Aust. Assoc. Sci.	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Res. Stud. State Coll. Washington	Research Studies of the State College of Washington.
Rev. Aluminium	Revue de l'Aluminium.
Rev. Chim. pura appl.	Revista de Chimica pura e applicada, Órgão de Sociedade Portuguêsa de Química e Física.
Rev. Fac. Quím. Ind. Agric.	Revista de la Facultad de Química Industrial y Agricola.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Mod. Physics.	Review of Modern Physics.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sborn. Trud. Ukrain. Chim. Inst. Odessa	Sbornik Trudov Ukrainskogo Nautschno-Issledova-Telskogo Chimitscheskogo Instituta Odessa.
Science	Science.
Sci. Agric.	Scientific Agriculture.
Sci. and Cult.	Science and Culture.
Sci. et Ind.	Science et Industrie.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Mem. Univ. Saratov	Scientific Memoirs of the University of Saratov.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Quart. Nat. Univ. Peking	Science Quarterly of the National University of Peking.
Sci. Rep. Hiroshima Tech. Sch.	Scientific Reports of the Hiroshima Higher Technical School.
Sci. Rep. Tôhoku	Science Reports, Tôhoku Imperial University.
Sci. Rep. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sci. Sect. Nat. Paint, Var. Assoc. Circ.	Scientific Section, National Paint, Varnish, and Lacquer Association, Inc., Circulars.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Scot. J. Agric.	Scottish Journal of Agriculture.
Seifens.-Ztg.	Seifensieder-Zeitung.
Sewage Works J.	Sewage Works Journal.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Heidelberger Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collection.
Soap	Soap.
Soap Trade Rev.	Soap, Perfumery and Cosmetic Trade Review.
Soil Res.	Soil Research.
Soil Sci.	Soil Science.
Sparwirts.	Sparwirtschaft.
Sprechsaal	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Stain Tech.	Stain Technology.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Steam Eng.	Steam Engineer.
Sugar Bull.	Sugar Bulletin.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Superphosphat	Superphosphat.
Superphosphate	Superphosphate.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tasmanian Agric. J.	Tasmanian Agricultural Journal.
Tech. Mitt. Krupp	Technische Mitteilungen Krupp.
Tech. Publ. Tin Res. Counc.	Technical Publications of the International Tin Research and Development Council.
Tech. Rep. Tôhoku	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.

Teer u. Bitumen	Teer und Bitumen.
Tekn. Tidsk.	Teknisk Tidskrift.
Textilber.	Melliand Textilberichte.
Tids. Kjemi	Tidsskrift for Kjemi og Bergvesen.
Tonind. Ztg.	Tonindustrie-Zeitung.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst Metals	Transactions of the American Institution of Metals.
Trans Amer. Inst Min. Met. Eng.	Transactions of the American Institute of Mining and Metallurgical Engineers.
Trans. Amer. Soc. Mech. Eng	Transactions of the American Society of Mechanical Engineers.
Trans. Amer Soc. Met	Transactions of the American Society of Metals.
Trans. Ceram Soc	Transactions of the Ceramic Society.
Trans. Dokuchaiev Soil Inst.	Transactions of the Dokuchaiev Soil Institute.
Trans Electrochem Soc	Transactions of the Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min Eng	Transactions of the Institution of Mining Engineers.
Trans Inst Min. Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. Inst Plast Ind	Transactions of the Institute of the Plastics Industry.
Trans. Inst Rubber Ind	Transactions of the Institution of the Rubber Industry.
Trans N. Eng Inst. Min Mech Eng.	Transactions of the North of England Institute of Mining and Mechanical Engineers.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Opt. Soc.	Transactions of the Optical Society.
Trans. Roy. Irish Acad	Transactions of the Royal Irish Academy.
Trans Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy Soc S. Africa	Transactions of the Royal Society of South Africa.
Trans Saratov Univ.	Transactions of the Saratov University (Gelehrte Notizen der Saratower Staats Universität).
Trop Agric.	Tropical Agriculturist (Ceylon).
Trop. Agric. (Trinidad)	Tropical Agriculture (Trinidad)
Tsch. Min Mitt.	Mineralogische und Petrographische Mitteilungen (Zeitschrift fur Kristallographie, Mineralogie, und Petrographie, Abteilung B).
U.S. Bur. Mines, Bull., Tech. Papers, and Rept. Invest.	United States Bureau of Mines, Bulletins, Technical Papers, and Reports of Investigations.
U.S. Bur Plant Ind.	United States Bureau of Plant Industry.
U.S. Dept. Agric. Bull. (or Circ)	United States Department of Agriculture Bulletins (or Circulars).
U S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
U.S.P.	United States Patent.
U S. Publ. Health Rep.	United States Public Health Reports.
Ukrain. Biochem. J.	Ukrainian Biochemical Journal.
Ukrain. Chem J.	Ukrainian Chemical Journal.
Union S. Africa Dept. Agric. Bulls.	Union of South Africa Department of Agriculture Bulletins.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exp. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verfkroniek	Verfkroniek.
Verh. Geol. Reichsanst. Wien	Verhandlungen der Geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Vermont Agric. Exp. Sta. Bull.	Vermont Agricultural Experiment Station Bulletin.
Vet. Rec.	Veterinary Record.
Virginia (Blacksburg) Exp. Sta. Bull.	Virginia (Blacksburg) Experiment Station Bulletin.
Virginia Truck Exp. Sta. Bull.	Virginia Truck Experiment Station Bulletin.
Welsh J. Agric.	Welsh Journal of Agriculture.
Wiss Veroff. Siemens-Werken	Wissenschaftliche Veröffentlichungen aus den Siemens-Werken.
Woch. Brau.	Wochenschrift für Brauerei.
World's Paper Tr. Rev.	World's Paper Trade Review.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.

Z. Biol.	Zeitschrift für Biologie.
Z. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Fleisch- Milch-Hyg.	Zeitschrift für Fleisch- und Milch-Hygiene.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Naturwiss.	Zeitschrift für die gesamte Naturwissenschaft.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Instrumkde.	Zeitschrift für Instrumentenkunde.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Parasitenk.	Zeitschrift für Parasitenkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzanernährung, Düngung, und Bodenkunde (*title now changed to* Bodenkunde und Pflanzenernährung).
Z. Pflanzenkr. Pflanzenschutz.	Zeitschrift für Pflanzenkrankheiten (Pflanzenpathologie) und Pflanzenschutz.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. pr. Geol.	Zeitschrift für praktische Geologie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Z. Ver. deut. Ing.	Zeitschrift Vereins deutscher Ingenieure.
Z. Ver. deut. Zucker-Ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie (*now changed to* Z. Wirts. Zuckerind.).
Z. Vitaminforsch.	Zeitschrift für Vitaminforschung.
Z. Wirts. Zuckerind.	Zeitschrift der Wirtschaftsgruppe Zuckerindustrie (Vereins der deutschen Zucker-Industrie).
Z. wiss. Biol.	Zeitschrift für wissenschaftliche Biologie.
Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuchtung	*Zeitschrift für Zuchtung.*
Z. Zuckerind. Czechoslov.	Zeitschrift für die Zuckerindustrie der Čechoslovakischen Republik.
Zavod. Lab.	Zavodskaja Laboratorija.
Zellstoff u. Papier	Zellstoff und Papier.
Zement	Zement.
Zentr. Bakt.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zentr. Min.	Zentralblatt für Mineralogie, Geologie und Paläontologie.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.

A DICTIONARY OF APPLIED CHEMISTRY.

B—*continued.*

BLACK ASH. The crude sodium carbonate of the Leblanc process, manufactured by heating a mixture of saltcake, coal and limestone:

(1) $Na_2SO_4+2C=Na_2S+2CO_2$

(2) $Na_2S+CaCO_3=Na_2CO_3+CaS$

BLACK B. (*Cibanone Yellow R*) *v.* ANTHRAQUINONE DYESTUFFS.

BLACKBERRIES. The fruit of the common bramble (*Rubus fruticosus*) probably including several sub-species. Kulisch (Z. angew. Chem. 1894, **7**, 148) gave the composition as:

Water.	Protein.	Acids.	Reducing Sugars.	Sucrose.	Ash.
84·9	0·5	1·4	6·5	0·5	0·6

American analyses, *e.g.* Munson, Tolman and Howard (U.S. Dept. Agric. Bur. Chem. Bull. 1905, No. 66), indicate more watery fruit with somewhat lower sugar content.

Average analyses of blackberry juice are given by Windisch and Schmidt (Z. Unters. Nahr.-Genussm. 1909, **17**, 584) as:

Sp.gr.	Solids.	Protein.	Acids.
1·038	9·9	0·34	1·5
Invert sugar.	Sucrose.	Tannin.	Ash.
5·77	0·21	0·13	0·42

The ash constituents include: K_2O 0·20, CaO 0·089, MgO 0·053, P_2O_5 0·069% (Kulisch, *l.c.*). The seeds yield an oil, reported by Krźiźan (Rev. Fett.-Harz-Ind. 1908, **15**, 7, 29) to show the following characteristics: sp.gr. 0·9256; saponification value 189·5; iodine value 147·8; Reichert-Meissl value 0; Hehner number 96·3. The liquid fatty acids, amounting to 91% of the oil, include 80% linolic acid and 3% linolenic acid. The solid acid is chiefly palmitic. Small amounts (0·8%) of phytosterol are also present.

Nelson (J. Amer. Chem. Soc. 1925, **47**, 568) examined the acids of the fruit and reported more than 80% of these to be optically active *iso*-citric acid, the remainder comprising *l*-malic and traces of oxalic, succinic, and citric acids. The pigment of the fruit was investigated by Vecchi (Chem. Zentr. 1914, [i], 1209).

A. G. Po.

BLACK BOY GUM *v.* BALSAMS.

BLACK CHALK. A brownish-black to blue-black carbonaceous shale; as a pigment it is inferior to the artificial carbon blacks.

BLACK FLUX. The residue of carbon and alkali carbonates obtained by igniting Rochelle salt.

BLACK GREASE. The crude fatty acids obtained by acidifying the soap stock made from cotton seed oil foots; they are usually distilled and separated into "olein," liquid, and "stearin," solid fraction.

BLACK HAW. The dried bark of the root of *Viburnum prunifolium*, Linn., a shrub growing in the central and eastern United States. It contains a bitter principle, *viburnin*, fat, resin, and tannin. The extract is used in the treatment of asthma.

BLACK HELLEBORE. Hellebore. The rhizome and roots of *Helleborus niger* L. (Fam. Ranunculaceæ), a herb cultivated in England and found wild in Central Europe. It contains two crystalline glycosides, *helleborin*, m.p. 269°, $C_{28}H_{36}O_6$ (Keller, Arch. Pharm. 1928, **266**, 545) and *helleborein*, but no alkaloids, and has strongly cathartic properties. White hellebore, *Veratrum album*, and green hellebore, *V. viride* (Fam. Liliaceæ), contain alkaloids causing effects entirely distinct from those of *H. niger*.

BLACKING. Blacking for shoes is mentioned as early as 1598, but it was not introduced into England until the reign of Charles II. It consists essentially of a black colouring matter, wax and some medium enabling the wax to be spread thinly over the leather.

Originally the black pigment used was some form of charcoal, but, in practice, this has now been abandoned in favour of nigrosine dye as such or in the form of its stearate or oleate.

The most satisfactory wax is, on the whole, crude carnauba wax, though this works best in conjunction with softer waxes which by themselves would not polish to a sufficient lustre. The admixture of other waxes also cheapens the product. The principal waxes employed are, in approximate order of hardness, carnauba wax, candelilla wax, shellac wax, crude montan wax, beeswax, ceresines, paraffins, japan wax and spermaceti. Synthetic substitutes for carnauba wax exist, but are mainly used for the light-coloured shoe creams, being too expensive for general use in the black preparations. The hard and soft waxes are usually mixed in about equal proportions, but blacking intended for use in hot countries contains more of the harder kinds, and the soft creams sold in tubes have a larger proportion of soft waxes. The total wax present amounts to about 25–30% of the blacking. Paraffin is very largely used, and to mixtures of this with a hard wax ozokerite is

often added, since it promotes uniformity, preventing the hard wax separating out in lumps (Ivanovsky, Farben Chem. 1933, 4, 85; Chem. Zentr 1933, I, 3860) Ozokerite tends to give soft pastes

The wax is made into a paste either by the use of an organic solvent or by partial saponification. The oldest, and still the commonest, solvent is oil of turpentine, which should be genuine balsam turpentine, not wood turpentine or pine oil (Ivanovsky, *l c*) Various cheaper solvents have been proposed, usually of the benzine or benzene types, and of these, lacquer benzine is the most important The essential qualities of the solvent are that it should dissolve all the waxes used and afterwards form a good emulsion, have a narrow boiling range and evaporate quickly enough for the wax layer to lose its stickiness and be capable of polishing very soon after application, but not so quickly as to dry up in the container, also, it must not damage the leather Turpentine is generally supposed to be actually beneficial to the leather, and, on that account, when other solvents are used a small proportion of turpentine or of a similarly scented substance is often added for purposes of sale Kuntzel and Malm (Seifens-Ztg 1935, 62, 535) carried out experiments to test the effect of turpentine and some of its substitutes on the life of leather subjected to bending, on its tensile strength, and on its porosity to air The results tended to confirm the superiority of turpentine owing to the fact that waxes dissolved in it tend to penetrate more deeply into the leather, whilst benzine and benzene tend to dissolve out the natural fat of the leather The beneficial effect of blacking is, however, mainly due to its action in keeping out water and the germs of decay

The usual method of manufacture of this type of blacking is to melt the waxes, beginning with that having the highest melting point and adding the others The temperature used should not be higher than is necessary for complete fusion, because otherwise there is risk of decomposition of the waxes and of undue loss by evaporation when the solvent is added The nigrosine base (about 3% of the whole) is then dissolved in an equal quantity of stearic or oleic acid at 70°–80° and stirred in The source of heat is then removed and the solvent added, at a temperature of 40°–50° in winter and less in summer To prevent the formation of lumps, the solvent must be added in small portions, stirring after each addition until the mixture is uniform To secure a uniform product, strict attention must be paid to the constancy of working conditions, including the temperature at which the blacking is poured into the containers.

A representative blacking of this type has the following composition:

25	parts carnauba wax (fat grey).
4	„ ceresine, 58°–60°.
8	„ paraffin, 50°–52°.
73	„ turpentine.
1·5	„ oleine
1·5	„ nigrosine base.

A higher proportion of wax may be used in the summer.

The blacking is sometimes sold in the form of sticks, which have the advantage of avoiding expensive packing and the use of a brush. Such products contain a larger proportion of wax, about 50% of the whole

Luxury shoe creams are made without paraffin

Saponified blacking is cheaper, because water replaces the organic solvent, but as might be expected, it is less resistant to water and may actually wash off and cause staining. In its manufacture the wax is melted and partially saponified by the addition of concentrated potassium carbonate Caustic potash must not be used, as any excess remaining in the finished product would be very harmful to the leather. Sodium carbonate is less satisfactory, since it tends to crystallise out when the blacking is kept in the cold The potassium carbonate may, however, be partially replaced by borax, which has the advantage of helping to prevent decay. The more acid waxes, such as japan wax and also rosin, are used to produce a soap, and the unsaponified portion remains suspended in the soap solution. Thorough stirring during manufacture is necessary both to secure proper dispersion and to prevent the mixture frothing over owing to the evolution of carbon dioxide. Instead of relying on the soap formed from the waxes, ready prepared soap is sometimes employed as an emulsifying agent. The colouring matter used is nigrosine, which is soluble in water, while its stearate is not.

A typical saponified blacking is made up as follows:

12	parts crude montan wax.
6	„ carnauba residues.
2	„ japan wax.
3	„ potassium carbonate, 96–98%.
77	„ water.
3	„ nigrosine.

A little glycerine is often added to prevent the blacking drying up, and a small proportion of formaldehyde, acetaldehyde, salicylic acid, or boric acid may be incorporated as a fungicide.

Mixed creams, being mixtures of the two types described above, are also made, but they do not appear to have any advantage other than that of cheapness.

BLACK-JACK. A miner's term for blende, or zinc sulphide (*v* ZINC, ZINC BLENDE)

BLACK LEAD. The common name of plumbago or graphite (*v* CARBON)

BLACKLEY BLUE. A triphenylmethane dyestuff

BLACK LIQUOR. Ferrous acetate (*v.* ACETIC ACID).

BLACK MUSTARD SEED OIL. The oil obtained from *Brassica nigra* (*Sinapis nigra*), has d^{15} 0 916–0 920, saponification value 174, iodine value 96–110 Used in soap-making.

BLACK POWDER. Ordinary gunpowder, a mixture of potassium nitrate (saltpetre), sulphur and charcoal.

BLACKSTRAP. The crudest molasses from sugar cane refining, formerly considered useless, is the chief raw material for nearly 90% of the industrial alcohol prepared in the United States.

BLANC DE FARD. Blanc d'Espagne (v. BISMUTH).

BLANC DE PERLE. Pearl White. Basic bismuth chloride prepared by precipitating bismuth nitrate solution with dilute hydrochloric acid. Used as a cosmetic. B.P.C.

BLANC D'ESPAGNE. Basic bismuth chloride precipitated by mixing solutions of bismuth nitrate and sodium chloride. Used as a cosmetic.

BLANC FIXE. Precipitated barium sulphate, used in the manufacture of paints and colour lakes.

BLANC PROCESS v. ALUMINIUM.

BLANKIT. Trade name for sodium hyposulphite, $Na_2S_2O_4$, formerly termed sodium hydrosulphite. Bleaching agent.

BLANQUETTE. A crude soda, less caustic than barilla, obtained at Aigues-Mortes by the incineration of *Salsola kali.*

BLAST FURNACE v. CARBON MONOXIDE.

BLASTING GELATINE. This is one of the most powerful explosives used in industry. It consists of a translucent jelly composed of 92 parts of nitroglycerin and 8 parts of nitrocotton containing about 12% of nitrogen. It is prepared by mixing the nitroglycerin with the dry nitrocotton, allowing the mixture to stand for some hours and then incorporating in a McRoberts or Werner Perkins mixer at a temperature of 40–45°C. The product is usually made up into cartridges by the use of a screw-filling machine. The gelatine is fed in through a hopper while the handle is turned, and the Archimedean screw then forces the material forward and out of the nozzle, the diameter of which corresponds with the core of the cartridge.

After manufacture, blasting gelatine continues to stiffen and if stored for any appreciable length of time tends to become less sensitive to detonation. It also shows a great tendency to exude nitroglycerin and to freeze if stored at a low temperature. This latter drawback has been removed to a great extent by substituting a portion of the nitroglycerin by dinitroglycol.

H. S.

BLAU GAS. The employment of liquefied gases as motor fuel has been known for many years and particularly for fuelling airship engines. Blau gas has been found a very satisfactory material for this purpose. It is obtained by high temperature cracking of a mineral oil, *e.g.* Scottish shale oil or gas oil, at a temperature of about 700°C. The product is freed from carbon dioxide and sulphur derivatives and compressed to 10 atmospheres, when a small amount of liquid separates. The gas is then further compressed to 100 atmospheres and yields a liquid consisting of methane dissolved in ethane, butane, propane, pentane and the corresponding olefines. This liquid contains 40% of the olefines and. in consequence, withstands very high compression ratios. Similar material is made from the lower hydrocarbons from petroleum, *e.g.* liquid propane containing a few per cent. of butane. This fuel has been used in the Graf Zeppelin. The term was originally applied to the gas discovered by Blau of Augsburg.

A. E. D.

BLEACHING. This term originally described the art of destroying the natural colour of vegetable and animal products without damaging them, but in practice the meaning of the term has been extended to include the whole process of purification in so far as this is chemical rather than mechanical in nature. The art acquires its greatest importance in connection with the textile fibres cotton, linen, wool and silk, and it is its application to these substances which will therefore be considered. Recent investigation has greatly increased our understanding of the principles underlying the art, and it can now be described in a much more scientific manner than was formerly possible.

COTTON.

Cotton is a seed hair composed in the dry state of about 90% of cellulose and 10% of substances which are regarded as impurities; the exact composition varies with the species and other circumstances. In industrial practice the hairs collected from the cotton seeds are given a mechanical cleansing to remove sand, leaf fragments, etc.; they are then drawn and spun into yarn, and finally, if desired, the yarn is woven or knitted into fabric. Bleaching is carried out as late as possible in the sequence of operations, for the reasons that the process is then cheaper, that cotton is more easily mechanically processed when unbleached, that processing after bleaching would inevitably soil the material, and that the bleaching can be more exactly adjusted to the purpose for which the goods are to be used. The greater cost of bleaching yarn as compared with cloth arises from the ease with which great lengths of cloth can be handled mechanically, and from the expense of the extra winding operations frequently required after bleaching yarn. Cotton is therefore bleached as woven cloth, and to a lesser extent as yarn; it is bleached in the loose unspun condition for the manufacture of cellulose esters and for surgical purposes.

A normal full bleaching process consists essentially of a steep to remove the starch added as size in weaving, an alkali boil (the kier boil or scour) to remove the bulk of the remaining impurities, a treatment with hypochlorite (the *chemick*) to destroy residual colouring matters, and an acid wash (the *sour*) to remove any remaining alkaline substances and to give a general cleansing. The properties of cellulose and of the non-cellulose constituents of cotton will be discussed with these processes in mind.

1. **Composition of grey cotton.**—The impurities in raw or grey cotton comprise mineral substances, nitrogen compounds, waxes and colouring matters, as well as other substances of which little is known. The cellulose content can be determined only by weighing the residue after the removal of impurities. This method, however, has given no precise results, as the more drastic the purifying method the greater is the loss of weight, and no definite end-point is reached by the most drastic methods that can safely be used. Column 2 of Table I gives the total losses in weight of various types of cotton when boiled with a 1% solution of sodium hydroxide at 20 lb. excess pressure, but the losses

are increased by about one-fifth if the concentration of sodium hydroxide is raised to 3% and the excess pressure to 40 lb Still more *drastic conditions result in decomposition* of the cellulose. It appears however, that the impurities amount in all to about 10% of the dry *grey fibre, varying* around this value according to the type of cotton. The composition of the impurities in these cottons, in so far as this is known, is given in the following table taken from the data of Fargher and Higginbotham[3]

TABLE I

NON CELLULOSE MATERIAL IN COTTON

Cotton	Total non cellulose constituents %	Mineral matter %	Nitrogenous material (N × 6 4) %	Wax and resin %	Residue of unknown composition %
Texas	7 3	1 1	1 1	0 5	4 6
Salsbury[1]	7 3	1 3	1 0	0 6	4 4
Tanguis	6 9	1 2	0 9	0 4	4 4
Sakel	8 1	1 2	1 7	0 5	4 7
Broach	*9 1*	*1 4*	*1 6*	*0 6*	*5 5*
Pima .	12 6	1 5	2 8	1 5	6 8

[1] Mississippi Delta

Grey cotton contains also fragments of seed *and leaf which have escaped the* mechanical cleansing processes, and oil and dirt picked up during spinning and weaving Cloth contains, in addition, the size which has been added to the warp to enable it to withstand weaving, and this size consists mainly of starch, fats, and waxes

2. Properties of cellulose.—Cellulose is slowly hydrolysed by the strong mineral acids yielding progressively simpler carbohydrates and finally glucose This progressive hydrolysis results in a steady fall in strength of the cotton hairs, and it is highly probable that the tensile strength of the fibre is dependent on the length of the chain molecules composing it. The chemically and physically modified materials obtained in the early stages of this hydrolysis are called hydrocelluloses. The process can be followed by measurements of the viscosities of solutions of the material in cuprammonium hydroxide under standard conditions. Unde*graded cellulose yields* solutions of very high viscosity, which, however, steadily decreases as hydrolysis proceeds. The viscosity is especially sensitive to the early stages of hydrolysis, and slight damage which could hardly be detected with certainty by a decrease in tensile strength, is readily revealed by the decreased viscosity. This measurement is the most general method of detecting and measuring slight degradation of cellulose, and has therefore become widely used in the control of bleaching operations.

Pure cellulose has little or no reducing power, and acid hydrolysis can be followed by the increasing amount of copper reduced by the hydrocellulose under standard conditions (the copper number). This also is a valuable measurement for the control of bleaching. Cellulose is not readily attacked by alkalis except in the presence of air, when oxidation occurs.

Oxidising agents attack cellulose fairly easily, and their use in bleaching must therefore be carefully controlled. The chemically and physically modified materials obtained in the early stages of attack are called oxycelluloses. Oxidising attack, like acid hydrolysis, results in a decreased viscosity and an increased copper number, and in general oxycelluloses are acidic. This acidity is measured most easily by the amount of the basic dye, methylene blue, adsorbed under *standard conditions. Alkaline* oxidising agents generally produce oxycelluloses of high acidity (methylene blue adsorption) and low reducing power (copper number), whilst acid oxidising agents yield substances of low acidity and high reducing power.

Degradation of cellulose, whether by oxidation or by acid hydrolysis, results in diminished tensile strength, changed dyeing properties, modified response to finishing treatments, and a tendency to yellow during storage or heating; such degradation must therefore be avoided during bleaching.

3 Properties of the non-cellulose constituents of cotton.—*The presence of fats* and waxes in cotton materials diminishes the wettability and affects the handle and the response to finishing treatments ; they are removed mainly to assist thorough and even penetration during dyeing and printing Both natural cotton wax and the fats and waxes used in sizing contain unsaponifiable as well as saponifiable substances The latter are readily hydrolysed by the alkali in scouring, but for the removal of the former reliance must be placed on emulsification.

The greater part of the mineral impurity is soluble in water, and practically the whole is removed by an acid wash.

The nitrogenous substances are partially soluble in water and dilute acids, and are removed almost completely by a mild alkali boil or a chemick.

Although pure cellulose has no reducing *properties, grey cottons of the types chiefly* used have copper numbers *varying from* 0·7 up to about 3, and the methylene blue adsorption is also much higher than that of pure cellulose. The impurities of unknown composition must therefore include reducing and acidic substances. A wash with water diminishes the copper number to 0 3–1 0, but the methylene blue adsorption is little affected ; this suggests that the reducing and acidic properties are possessed in the main by different substances. A mild alkali boil is sufficient to reduce the copper number to 0 1, but a more thorough treatment is necessary before it becomes too small to detect with certainty. The methylene blue adsorption may be diminished to about half of its initial value by *boiling with water at 20 lb. excess* pressure, and this is accompanied by some loss of weight. Progressive increases in the severity of the scour, up to a boil with a 3% solution of caustic soda at *40 lb.* excess pressure, result in progressively lower values of the methylene blue adsorption and in progressively greater losses in weight. Boiling at higher temperatures results in decomposition of the cellulose. The continuous fall in methylene blue adsorption is some evidence that the progressive loss of

weight is due to the dissolution of less resistant substances rather than to the decomposition of cellulose and the dissolution of the decomposition products. The methylene blue adsorption may be diminished to 20% or less of its initial value, and the total loss of weight increased to 9–15% depending on the type of cotton. Whether a part of the loss of weight is due to substances which are neither reducing nor acidic is not known, but it is probable that no sharp line could be drawn between some of the more resistant impurities and cellulose itself. The impurities which are removed in the scour are less stable than pure cellulose and their removal results in a lessened tendency to yellow when goods are stored or heated.

4. **Cotton bleaching operations (hypochlorite bleach).** (*a*) *Singeing and Steeping.*—The first treatment given by the bleacher after the receipt of woven goods is singeing. In this process the cloth, the pieces of which have been sewn end to end, are passed over red-hot copper plates or through rows of gas burners. The surface hairs are burnt off thereby from either one or both faces, and the cloth presents a smoother, less fluffy appearance. After singeing it generally passes into water, and is given a steeping process which aims primarily at the removal of the size. If water alone is used for steeping (rot steeping), it should be heated to 35°–40°; organisms naturally present in the water then multiply rapidly and secrete starch liquefying enzymes, so that when the cloth is washed after a day's treatment a large proportion of the starch and some part of the impurities natural to the cotton are removed. The process is both faster and more thorough if an amylolytic enzyme is added to the water, but care must be taken to ensure the correct temperature and p_H for the particular enzyme used. Under the most favourable conditions the action of the enzymes is complete in about 20 minutes, and with the aid of suitable apparatus the process may be made continuous. An alternative procedure is to steep in warm 0·5–1·0% sulphuric or hydrochloric acid solution. This process is especially desirable if an ash-free fabric is required, and it has the further marked advantage of resulting in an improved white after a subsequent alkali boil. By a suitable choice of concentration and temperature it is possible to hydrolyse the starch sufficiently rapidly to make the process continuous. Yarn, being free from size, is not steeped, but it is sometimes gas singed.

(*b*) *Scouring.*—After washing subsequent to the steep the cloth passes to the kier boil or scour. This aims at removing all the impurities from the fabric and at so improving its colour that only very mild oxidising conditions are necessary in the chemicking process. For a thorough bleach a caustic alkali must be employed, and in practice the choice lies between caustic soda and lime. When lime is used insoluble lime soaps are formed from the saponifiable fats, and this boil must be followed by a sour to liberate the free fatty acids and a soda ash boil to dissolve them as sodium salts, with, of course, intermediate washes. The lime-soda ash process has the advantages over the caustic soda process that the chemicals are cheaper and that it produces a rather clearer and brighter white. On the other hand, the caustic soda process requires only a single boil, and, moreover, residues of lime are undesirable in cloth for dyeing or printing. The concentration of lime in the scouring liquor is limited by its small solubility, and in order that sufficient may be present for effective scouring the goods are impregnated with milk of lime during their passage to the kier. Lime neutralised during the scour is then replaced by the dissolution of a further amount.

During the boil the nitrogenous substances are removed readily, but a thorough treatment is necessary to diminish to minimum values the amounts of fat and wax and of reducing and acidic substances. The efficiency of the scour may therefore be assessed by measurements of fat and wax content, of copper number, of methylene blue adsorption, and of whiteness, as well as of wettability, which is dependent on the wax content. The following table taken from the data of Fargher and Higginbotham [3] compares the results of various single boiling treatments.

TABLE II.

COMPARISON OF BOILING TREATMENTS WITH AN AMERICAN COTTON.

Treatment.	Scouring loss %	Properties of Scoured Cotton.			
		Wax %	Nitrogen %	Copper number.	Methylene blue adsorption.
Untreated	—	0·49	0·194	1·15	—
Water at 25°	2·4	0·49	0·127	0·34	—
6 hours' open boil :					
With 0·7% lime	5·0	0·40	—	0·08	1·22
With 1·3% Na_2CO_3	5·1	0·49	—	0·08	1·17
With 1·0% NaOH	5·2	0·36	—	0·03	1·10
6 hours, 20 lb. pressure :					
With water	4·2	0·48	0·085	0·17	1·50
With 0·7% lime	6·1	0·28	—	0·09	1·12
With 1·3% Na_2CO_3	6·6	0·31	—	0·07	0·87
With 1·0% NaOH	7·0	0·20	0·03	0·01	0·86

During the boil alkali is neutralised, both in saponifying fats and in combining with acidic impurities or decomposition products, and sufficient caustic must be taken to ensure an excess at the end of the boil. Soaps, pine oil, and many proprietary substances are recommended for addition to the kier liquor to assist thorough penetration of the material and emulsification of unsaponifiable waxes, and these are used to some extent. In many processes two or more boils are given, and it is then usual to insert between boils not only a wash but also a sour and sometimes a chemick. The second and any subsequent boils are often milder than the first, the caustic being replaced by soda ash or even by soap, or the boil conducted at atmospheric pressure. If air is allowed access to material wet with alkali, oxidation occurs, and it is therefore essential to keep the cotton entirely below the surface of the liquor.

(c) *Chemicking.*—The purpose of chemicking is to destroy the natural colouring matters which are always present in raw cotton and which are only partially removed by the previous processes. It consists of a treatment in the cold with either *calcium or sodium hypochlorite.* This treatment involves unavoidably some oxidation of the cellulose, and this oxidation must be kept at a minimum by careful control of the operation. It is for this reason that as good a white as possible should be obtained in the scour, in order that the chemicking treatment may be light.

Successful chemicking depends on the control of the p_H of the liquor. Commercial solutions of hypochlorites contain free caustic alkali, as do also extracts of bleaching powder, and after suitable dilution the p_H is generally about 11. The oxidation of impure cellulose results in the dissolution of acidic organic substances and in the reduction of strongly alkaline sodium hypochlorite to neutral sodium chloride; the p_H therefore falls. If the p_H becomes too low the rate of attack of cellulose is increased; it is much greater at p_H 7 than at p_H 11, and if the chemick becomes approximately neutral serious damage may be done to the material. In this respect sodium hypochlorite has an advantage over calcium hypochlorite, as the p_H of the former can be buffered at a suitable value by the addition of soda ash. Calcium hypochlorite cannot be buffered in this way, and, moreover, generally contains less free alkali on account of the small solubility of calcium hydroxide. Attack of cellulose is faster also at higher temperatures and at higher concentrations of hypochlorite. The correct initial concentration depends on the thoroughness of the preceding scour and on the ratio of chemick liquor to cotton, and it should be chosen so that only a small excess is left at the end of the operation. The impurities are much more rapidly attacked than is the cellulose; when the initial concentration is suitable it rapidly falls to a low value, and the cotton can then be safely left for some hours to ensure completion of the process.

5. Cotton bleaching plant. (a) *The Kier.*—Cotton scouring is conducted in large iron boilers or kiers, the usual capacity of which is 1–4 tons of cotton; the form depends on the structure of the cotton material and on whether the scour is to be under pressure or open. The important features are the means of maintaining the correct temperature and of securing relative movement between the liquor and the cotton and thus adequate treatment of all parts of the latter. Heating by steam, either open or closed, and continuous movement of either liquor or material are universal.

A simple form of kier is that illustrated in Fig. 1 and made by Messrs. Jackson and Brother.

It consists of an upright cylinder closed at the bottom, and provided with a false bottom and a vertical pipe up the centre. The cotton is piled on the false bottom and covered with liquor. Live steam is then blown in through the pipe at the bottom and forces the liquor up through the central (or puffer) pipe and on to the top of the cotton; even distribution is assisted by a spreader. The liquor percolates through the cotton and returns to the space below the false bottom. The steam is liable to lift the charge of cotton and to keep this below the surface of the liquor and out of contact with the air it is held down by chains secured to the wall of the kier. This form of kier is suitable for mild scouring processes.

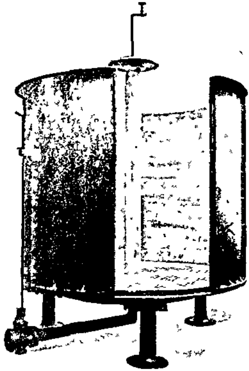

FIG. 1.

In kiers for scouring under pressure it is more usual to circulate the liquor through the kier and through an external heater by means of a pump, and the heater is supplied with closed steam. A kier of this type, made by Messrs Mather and Platt, is illustrated in Fig. 2.

When live steam is used the liquor is continuously diluted by its condensation, and the original charge must be small and concentrated. Closed steam has the disadvantage that the heating up of the kier is slow, and kiers are in use which aim at combining the advantages of these two forms of heating. Advantages are claimed also for devices which automatically supply liquor intermittently instead of continuously to the top of the kier. In Gebauer's kier the liquor is fed into a narrow annular space between the outer wall of the kier and an inner perforated cylinder, and the circulation is horizontal from this annular space, through the cotton, and into a central perforated pipe.

In filling these kiers, yarn, in whatever form

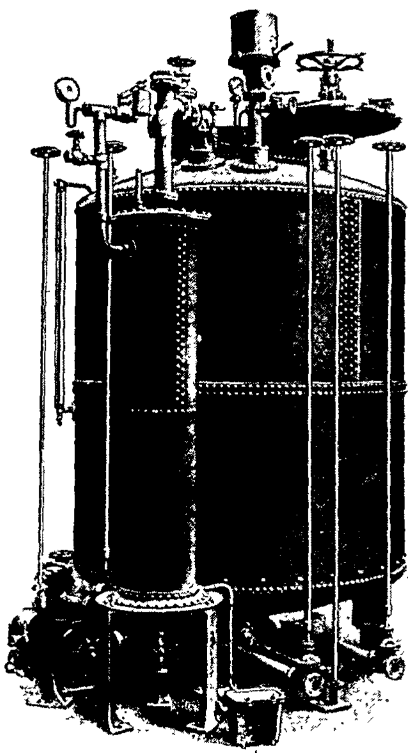

FIG. 2.

it may be, is packed in by hand and carefully trodden to a uniform density, so that liquor penetration will be thorough. Cloth is fed in as a continuous rope of pieces sewn end to end, and also must be carefully packed. A machine for piling cloth is illustrated in Fig. 3, the cloth being fed in at the top of the apparatus and emerging at the bottom. The lower end of the tube is given a mechanical motion such that the cloth is piled uniformly over the cross-section of the kier.

The wagon kier, Figs. 4 and 5, is horizontal, and the goods are packed into two trucks CC, which run into the kier on rails. The kier is then closed with the hinged door A, the wagons are each divided into two compartments by central perforated partitions, the liquor is circulated by the centrifugal pump B, and passes through the perforated partitions and horizontally through the cloth. Two pairs of trucks are provided, and the second pair can be run in with a further load of material as soon as the first pair is run out. The long time usually required to empty and refill a kier is saved, and operation is almost continuous.

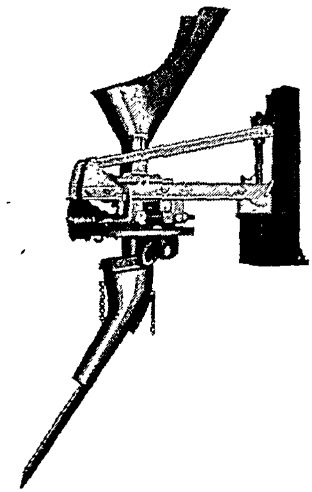

FIG. 3.

Many cloths cannot be bleached in rope form without developing fold marks or other faults which cannot be removed subsequently. They must therefore be boiled in open width in kiers designed for this purpose. The commonest

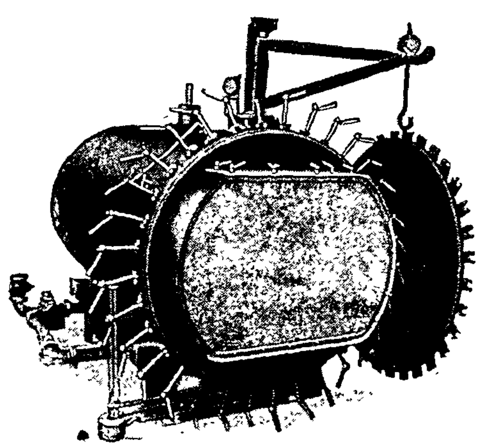

FIG. 4.

of such kiers is the Jackson kier, illustrated in Fig. 6.

The cloth is impregnated with the alkali and batched up on one of two rollers on a special frame which is run into the kier; the latter is then closed and filled with caustic. The ends of the rollers engage with winding

piled down for several hours to complete the chemicking process. When chemicking and souring are done in this way the cloth is sometimes steeped in the continuous piler illustrated in Fig. 9.

The cloth is fed in through the top and fills the apparatus. The bottom consists of a series of rollers; these facilitate the passage of the cloth, which finally emerges at the lower end. The capacity of the apparatus is such that each element of cloth remains in it for about 20 minutes. One such passage is sufficient for souring, but two machines in tandem are generally used for chemicking.

Cloth in open width may be handled in several ways. One form of plant, made by Messrs. Jackson and Brother, is illustrated in Fig. 10.

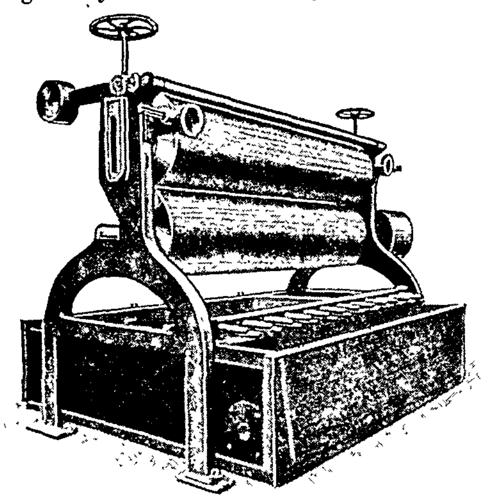

FIG. 8.

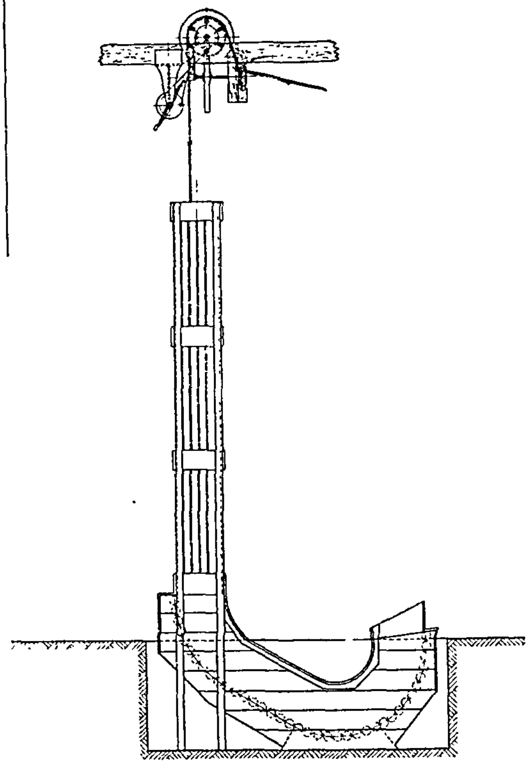

FIG. 9.

In its passage between two batch rollers, one of which is seen in the illustration, the cloth passes round the upper rollers, and is sprayed with chemick supplied through perforated pipes at the top of the apparatus. The chemick and acid are stored in separate wells below the floor level.

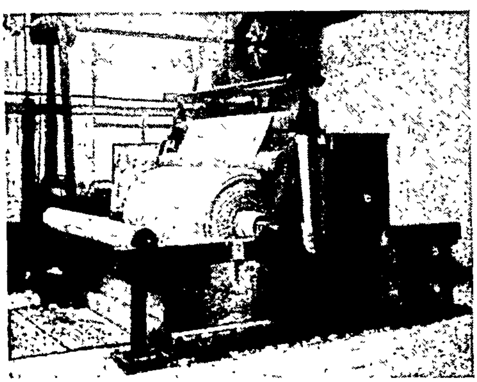

FIG. 10.

Alternatively the chemick is contained in one or more tanks, and the cloth is guided through it by several pairs of rollers, one of each pair being deeply immersed in the liquor and the other near to or above the surface. Each tank is provided with a few pairs of rollers and with a mangle through which the cloth passes when it leaves the tank. After passage through the machine the cloth is folded or rolled and left for several hours or overnight; it is then washed, soured, and washed in similar apparatus.

Yarn packages such as cops are usually treated in the percolating type of apparatus, and for this purpose they are often packed in bags before piling on to the false bottom. Machines are also available in which each package is placed on a hollow perforated skewer forming part of the apparatus. The chemick is pumped through the packages, either entering or leaving them through the skewers, and in this way thorough penetration is ensured.

(c) *Continuous Systems.*—The types of plant so far described for scouring and chemicking are designed for essentially batch processes. A number of continuous processes for the bleaching of cotton have been described and are probably in use to a limited extent. In all such processes the treatments, especially the scour, must necessarily be much briefer than in the normal batch processes, and it is therefore unlikely that the cellulose can be so thoroughly purified. When thorough scouring is unnecessary continuous processing becomes more practicable, and a boiling process of this type

is used on a considerable scale for cloth. The cloth is guided by rollers through a series of tanks containing the heated alkali, which may be caustic soda, soda ash, or trisodium phosphate, the last named is not uncommonly used in America

6. **General considerations in cotton bleaching.**—The bleaching treatment given to cloth depends on the purpose for which it is to be used. When cloth is to be marketed white and finished without the aid of filling materials, the desired handle is obtained solely by mechanical means. A good response to these mechanical finishing treatments requires the utmost purity in the cloth. A good and permanent white also necessitates freedom from impurities and from oxycellulose which may be produced during chemicking. For such cloth the scour must therefore be thorough, both in order to secure the maximum removal of impurities and in order that a good white may be obtained with only a mild chemicking process. For this purpose the lime soda ash scour is often preferred as rather more brilliant whites are obtained than are possible by the caustic soda process. Whether lime or caustic soda is used the details of the process vary considerably from works to works. Typical conditions for the lime scour are boiling the cloth for 6–12 hours at 20 lb excess pressure with 35–60 lb of lime per ton of cloth, followed by a similar boil with about the same weight of soda ash sometimes with the addition of rosin or other soaps. When caustic soda is used the concentration of the liquor is 1–2%. If sufficient purification has not been effected by the lime and soda ash boils the latter may be repeated, and a sour and often also a chemick is inserted between the boils. The caustic soda boil also is often repeated a second time, and a chemick and sour, a sour alone, or only a wash inserted between the boils. The number of boils required depends on their efficiency, and is increased if pressure kiers are not available. The present trend is away from long processes including many successive treatments of the fabric, and towards the use of a few efficient and carefully controlled operations. It will be clear from what has been said already that if the scour has not been sufficiently thorough it is unwise to attempt to get a good white by more severe chemicking; a good white can indeed be obtained, but its permanence will be inferior owing to the formation of oxycellulose.

When cloth is to be used for calico printing the whiteness required depends somewhat on the character of the print; for pale and bright shades a good white is important. In all cloth for printing the white must be stable so that it will not yellow during the steaming to which it will be subjected. Further requirements are a high and uniform adsorbency and freedom from impurities which may act as mordants for certain classes of dyes which are used in printing. Thorough purification of the cloth by an efficient scour followed by a carefully controlled and mild chemick is therefore demanded.

The bleaching treatment required by cloth for dyeing varies more widely with the colour to be used, as there is no uncovered white ground as in printing. For dark and dull shades uniform adsorbency is often all that is necessary, and a mild scour with soap or soda ash or with both soap and soda ash may then suffice without a chemick. For pale and bright shades the requirements approach those for printing cloth.

In certain cases, for example, shirtings containing coloured stripes introduced during weaving, goods containing dyes have to be bleached. It is then essential to avoid damaging the colour or transferring it from coloured to uncoloured parts of the goods. Few dyes can withstand a boil with caustic soda; soda ash, soda ash and soap, or soap alone must therefore be used for scouring, according to the fastness of the dyes. More dependence must then be placed on the chemick to secure the desired degree of white. The presence of dyes, however, necessitates special care in chemicking in order to avoid injuring the shades. Careful control of the p_H is particularly important, as many dyes which are little affected by dilute hypochlorites at p_H 11 are greatly changed in colour if the solution approaches neutrality.

7. **Peroxide bleaching of cotton.**—In recent years there has been a considerable increase in the use of peroxides as oxidising agents in place of hypochlorites. This has been especially the case in Germany and in America, and this replacement has been facilitated by the manufacture of stable 100 volume hydrogen peroxide. For bleaching cotton this is diluted with the addition of a mild alkali such as sodium metasilicate or sodium phosphate. Sodium peroxide is used in a similar manner, but it is dissolved in an equivalent amount of sulphuric acid or the solution in water is neutralised with sulphuric acid before the addition of the mild alkali. The bleaching operation is carried out at or near the boil in an ordinary kier. The kier must, however, first be lined with cement and sodium silicate or with a similar preparation, because in the presence of heavy metals cotton is rapidly destroyed by hydrogen peroxide.

When the sole bleaching treatment given to the cotton is a boil with peroxide and sodium silicate there is a considerable conservation of weight as compared with a caustic soda or a lime soda ash bleach. The goods are, however, less wettable and the white is poorer; they can have, therefore, only a limited application. When the peroxide treatment is preceded by a pressure caustic soda boil the cost is greater and the advantage of a conservation of weight is lost; the goods can, however, still be scoured and bleached in the same vessel, and this results in some economy of handling and in a fuller utilisation of the plant.

Peroxide bleaching has a marked advantage for the bleaching of coloured stripe goods. The vat dyes commonly used for these stripes are liable to bleed during an ordinary scour because they are reduced to the soluble leuco compounds by impure cellulose in the presence of alkali. Such bleeding is avoided when the scour and bleach are combined by the addition of a peroxide to the kier liquor. The value of this procedure is one of the causes of the recent rapid progress of the peroxide method. Where this process is used for coloured goods it is likely to be

extended also to whites in order to avoid the use of two separate processes, and this may be a reason for its extensive use for white bleaching in America. It is probable that hypochlorite bleaching is more efficiently carried out in the British cotton industry than elsewhere, and this fact, together with the high quality of the bleach demanded for a large proportion of the goods and the higher cost of peroxide as compared with hypochlorite, may be responsible for the comparatively infrequent use of peroxides in this country.

Linen.

Linen, like cotton, is composed essentially of cellulose. It is, however, a bast fibre comprising about 75% of withered flax stems, and the various fibres in the stem have first to be separated from one another and from the remainder of the stem by a process of *retting*. This usually involves bacterial action; an alkali boil separates the fibres much more rapidly, but also removes natural wax and renders the flax more difficult to spin. When retting has proceeded far enough the fibres are separated by processes of beating (*scutching*) and combing (*hackling*), and are then ready for spinning. In this condition linen contains about 30% of non-cellulosic material consisting of waxes, proteins, pectins, lignins and hemicelluloses. Green linen is thus much more impure than is grey cotton ; moreover, the fibres, unlike cotton hairs, have no cuticle, and this apparently renders them more liable to chemical attack. These factors condition the differences between the processes of bleaching linen and cotton, both of which aim at removing impurities from crude cellulose.

Linen cannot withstand the high pressure caustic soda boils used for cotton ; the pressure is limited to 5–10 lb. and for yarn the alkali is restricted to sodium carbonate containing 10% of caustic soda. The whole of the impurities cannot be removed by one " turn " of the cycle—boil, chemick, sour—and for a full bleach at least three turns are required. The chemicking process in the first turn for linen yarn differs in essential particulars from cotton chemicking. The hanks are placed on square wooden reels over the tanks, so that their lower ends dip into the chemick. The reels are slowly revolved, the direction of rotation being automatically changed at regular intervals. The yarn is thus alternately exposed to the chemick and to atmospheric carbon dioxide, and the liquor tends to become less alkaline. Since cellulose is rapidly attacked by chemick when nearly neutral it is probable that this process is occasionally responsible for damage to the linen. It appears likely that one function of this reeling process is a chlorination of ligneous impurities, resulting in their dissolution in a subsequent alkali boil ; chlorination would be assisted by acidification of the chemick. Lunge proposes to acidify with acetic acid instead of with carbon dioxide, to avoid the precipitation of calcium carbonate. Reeling must be carefully conducted or the yarn becomes *slayed* (hairy) and is then difficult to wind. The process is not repeated a second time, subsequent chemickings being steeping processes.

The grassing of linen, that is, its exposure to the weather in fields for several days, is still commonly practised, though its use is diminishing. This treatment is interposed between the boil and the chemick, but its function is not clear.

The chemical control tests used for linen bleaching are somewhat different from those used for cotton. The viscosity test is not so easily carried out, as the large amount of insoluble impurities necessitates the filtration of the solution of linen in cuprammonium. For this reason the degree of chemical degradation is frequently measured by the solubility in caustic soda at 15° under standard conditions. This measurement is easier than that of viscosity, but is stated to be less reliable. The quantity of non-cellulosic substances remaining is measured by the alkali solubility number, that is by the percentage dissolved by boiling caustic soda under standard conditions. Raw linen reduces alkaline copper solutions, and a high copper number may therefore be due to residual non-cellulosic substances, or to degradation of the cellulose, or to both causes.

Linen Yarn Bleaching.—Complete purification of linen results in a loss of weight of 25–30%, and many processes are therefore in use which aim at conserving a part of this weight whilst giving as good a quality of material as is then possible.

For the highest quality of fabric the linen is boiled as yarn and the bleaching is completed after weaving. In the boiling process soda ash containing 10% of caustic soda is used. The kiers are similar to low-pressure cotton kiers, and are operated at about 5 lb. excess pressure. After boiling, the yarn is washed in the kier, and the loss of weight at this stage is 15–20%.

The process of " creaming " aims at a minimum loss of weight. Yarn so treated is used for poorer qualities of cloth, and receives only a light bleach after weaving. The yarn, after being boiled for an hour with about 5% of soda ash containing 10% of caustic soda, is washed and reeled, and the resultant loss of weight is about 10%. For intermediate qualities of cloth the yarn bleaching process is carried further. For half, three-quarter and full whites the yarn after treatment as described above is reboiled in a weaker alkali solution (scalded) and re-chemicked by steeping. These processes may be repeated, and the desired whiteness is obtained by varying the severity of the treatments and the number of repetitions. For a full white the loss of weight is about 20%.

Linen Cloth Bleaching.—When bleached as cloth, linen can be somewhat more drastically treated than is advisable for yarn, and for the first boil either lime or caustic soda is used. When lime is used it must be followed by a sour and a soda ash boil, as with cotton. Cloth is always chemicked by a steeping process, and the plant used for boiling, chemicking, and souring is similar to that used for cotton.

A full bleach for cloth woven from unboiled yarn consists of the following sequence of operations:

1. Low pressure lime or caustic soda boil.
2. Sour.

3 One or two low pressure boils with caustic soda and resin soap, caustic soda alone, or soda ash
4 Grass for 2–7 days according to the weather
5 Chemick
6 Sour
7. Low pressure boil with caustic soda or soda ash.
8. Grass
9 Chemick

If necessary, the cloth may then be rubbed between boards to remove undestroyed brown particles of ligneous matter (*sprits*), and the operations of grassing chemicking and souring repeated The fabric is well washed between each chemical treatment

When the cloth has been woven from bleached yarn the cloth bleaching processes are reduced in number and severity according to the thoroughness of the yarn bleaching process and the quality of cloth required

The half bleaching processes so far considered conserve weight at some sacrifice of the quality of the linen A process patented in 1923 [1] claims to reduce the loss of weight by half without adversely affecting the stability of the white or the wearing qualities of the material. This is achieved by removing thoroughly the waxes, proteins, pectins and lignins by special processes, but leaving the hemicelluloses Oils, fats and waxes are removed by extraction with an organic solvent, and the goods are then scoured with lime or with a caustic alkali in the cold or at a temperature below the boiling-point Normal methods of chemicking are used. Processes of this type are now worked on a considerable scale, and the resulting material finds a wide application

Wool

In its natural condition wool contains a large proportion of foreign material, and this is generally removed by a scouring process before the mechanical treatment of the fibre begins To facilitate the processes leading to the conversion of the loose wool into yarn the fibre is oiled, and yarn which is not to be used for weaving is therefore frequently re scoured Cloth also needs to be re-scoured because it is generally woven from unscoured yarns and the warp size has also to be removed. The final whitening or true bleaching process is carried out on the scoured yarn or cloth

The total amount of impurities in raw wool is very variable, and figures ranging from 15% to 80% of the weight of the fleece are given. These impurities consist partly of dirt, earth and vegetable matter, and partly of *yolk*, this last being material secreted by the animal. The amount of yolk varies considerably, and it sometimes exceeds the weight of the purified fibre. This secretion is readily divided into two parts, namely, the portion which is soluble in water and is known as *suint*, and the wool fat.

Suint is dried wool perspiration, and consists in the main of the potassium salts of a variety of aliphatic acids and of potassium carbonate.

Wool fat is insoluble in water but soluble in most organic solvents It consists of the cholesterol and *iso*cholesterol esters of fatty acids, as well as of a certain proportion of these alcohols and acids in the free state. The melting-point is 40°–45°; it is saponified only with difficulty but is easily emulsified.

Purified wool fibre consists chiefly of keratin, though apparently it contains also 1–2% of wool gelatin, soluble in hot water. Keratin is a protein, and contains a small and variable percentage of sulphur. When heated with water wool becomes soft and plastic, and it is dissolved by boiling dilute caustic soda. Even sodium carbonate weakens the hairs and spoils their appearance unless it is cool and dilute, but weaker alkalis such as soap, ammonia and ammonium carbonate have no action at ordinary concentrations. Wool is comparatively resistant to acids.

Loose-wool scouring.—The object of scouring loose wool is to remove the yolk, dirt, etc., and so leave the fibre in a better condition for spinning and subsequent processes When wet, wool is easily felted or matted, and on this account it must be kept as open as possible and mechanical handling must be limited in amount and suitable in character, frequent squeezing is not permissible Wool fat cannot be saponified by any process that can be applied to wool, and it is therefore removed either by emulsification with weak alkalis such as soap or by solvent extraction Much of the dirt is cemented to the fibre by the wool grease and falls off when this is removed.

Scouring with Soap.—Loose wool is usually scoured with warm soap solutions, which dissolve the suint and emulsify the wool fat. The suint may, however, be removed previously by a warm water wash. This procedure has the advantage that the scouring liquor is less rapidly fouled, but it introduces an extra operation with its attendant costs The wool is washed in several portions of water operated on the counter current principle, or the water may be sprayed on to the wool supported on a travelling lattice. By evaporating the wash water and calcining the residue, potassium carbonate, containing only a small proportion of the sodium salt, is obtained. The process has the further advantage that loose dirt is removed, and the formation of an emulsion in the soap solution is thereby facilitated.

Scouring is performed in a series of long rectangular vessels, termed wash-bowls, 30–40 ft. in length and holding up to 2,000 gallons of liquor. The essential features are a device for feeding in the wool, an inner tank with a false bottom or perforated walls to allow heavy dirt to escape, a system of mechanically operated rakes to move the wool slowly along the bowl, and a pair of squeeze rollers at the exit end to express most of the dirty liquor from the wool. One such bowl is illustrated in Fig. 11. It consists of a rectangular trough A, with a light frame B suspended over it by chains and carrying a series of transverse, fixed, vertical rakes or combs C. The wool, either in its raw condition or after steeping, is spread evenly on the moving endless apron or feeder D; thus it is introduced continuously at one

end of the trough. By suitable mechanism the frame is lowered, and the wool is pressed at once beneath the surface of the scouring liquor by the perforated tray or sieve E. When the frame is lowered sufficiently it moves forward, the rakes carrying the wool gently towards the other end of the bowl. When the forward stroke is completed, the frame is lifted up, the rakes rise vertically out of the liquid, and the frame returns to its original position. By these successive movements the wool is passed slowly through the scouring liquor. At the delivery end it is carried up the inclined plane F by the rakes fixed on the small frame G, which is hinged to the larger one. Having been pushed over the ridge, the wool slips down between the squeezing rollers HH, ready to be passed through a second similar bowl.

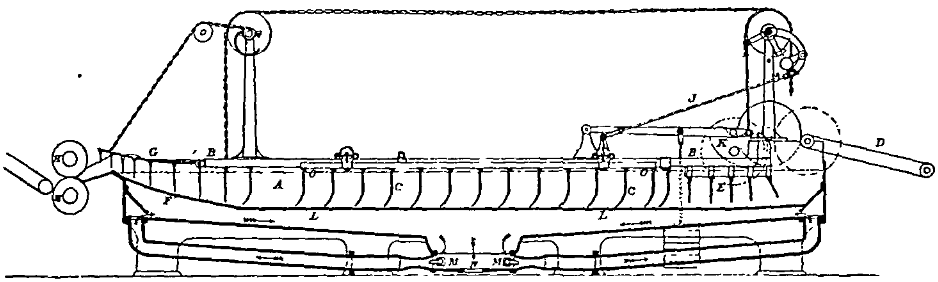

FIG. 11.

The working of the machine as described above is suitable for Botany and other fine classes of wool. When washing low Cape, River Plate and similar wools, which contain much dirt and sand, an additional movement is given to the rakes while in the liquor. This is effected by having the rakes fixed in a second frame OO, which receives a slight backward and forward movement by means of the rod O and the cam K during the inward movement of the main frame BB, to which it is attached. By this means the wool is opened out slightly and agitated, and the sand and dirt fall through the perforated grating LL. When the scouring liquor becomes too much soiled for further use, the steam injectors MM are brought into action in order to stir up all the sediment, and the dirty liquor is run off by the plug hole N. Many modern machines are provided with means of discharging the dirt from the bottom continuously. Generally three or more such bowls are placed in line so that the wool passes automatically from one to the other.

The soap used in scouring must be soluble and have a high emulsifying power ; it should be free from an excess of either alkali or fat. Additions of soda ash are frequently made to the bath, but it is preferred to start with a neutral soap and to make any additions that may be necessary. Olive oil soaps are probably the best, but soaps from other oils and fats are also in use. The water should be soft.

The compositions of the scouring liquors depend on the number of bowls, the quality of the wool, and the amount of impurities to be removed. If only three or four bowls are available the first may contain 0·5–1·0% soap solution. Generally soap alone is inadequate for efficient scouring and some sodium carbonate is added ; this increases the emulsifying power, but the emulsions formed are less stable. Most waters are more or less hard and earth dirt also tends to precipitate soap ; some addition of alkali is advisable on these accounts. The scouring temperature should not be above 60°, but it appears to be desirable that it should be as high as the melting-point of the wool fat, namely, 40°–45°, and this is especially so when much fat is present. In general the finer the wool the lower should be the temperature and the smaller the amount of sodium carbonate. The conditions should be as mild as is consistent with efficient scouring. Excessive scouring results in partial hydrolysis of the keratin, loss of sulphur, modified affinity for dyes and diminished strength. Probably there is always some loss of strength, but this should be kept at a minimum. Formaldehyde or other substances are added sometimes as protective agents. When five or six bowls are available and the wool has not been washed it may be preferable to have sodium carbonate only in the first bowl, as the presence of much dirt tends to break soap emulsions.

In the later bowls the temperature is often lower than in the first, and the last bowl contains rinsing water at about 30°. Thorough washing is necessary as any alkali left in the wool results in yellowness. When more than one bowl contains soap and sodium carbonate these may be operated on the counter-current principle.

Wool removed from the skin by liming, that is, *slipe* wool, always contains lime, and preferably it is washed with acid before scouring. If this is not done the precipitation of lime soaps may be avoided by the addition of sodium metaphosphate to the scouring liquor, or by using only sodium carbonate and a little caustic soda in the first bowl.

Suint Scouring of Wool.—It has been stated that suint consists chiefly of the potassium salts of aliphatic acids, and it may be used to replace soap in scouring. In this process at least four bowls are required. In the first two no soap or soda ash is used and the temperature is 60°. At this temperature the wool fat emulsifies, and about half of the fat is removed in the first bowl and a further quarter in the second. The third bowl contains a weak soap solution and

removes the remainder of the fat, whilst the last bowl is a water rinse As far as possible the composition of the liquid in each bowl is kept constant, and a continuous system is therefore preferable to one in which the bowls are emptied and refilled periodically The liquor from the first bowl is purified and returned to the system Purification may be effected by centrifuging, but this is expensive In another method sedimentation is assisted by de aerating the liquid by exposing it to a vacuum, and an amount of acid is then added which is insufficient to precipitate the whole of the organic acids The liquor is then neutralised before re use

As compared with wool scoured with soap and soda ash, wool scoured with suint in a con tinuous system is stated to be brighter and whiter, and to be more free, open and lofty The cleaning is more uniform and less attention is required, and there is an economy in soap and alkali

Scouring Wool with Volatile Solvents—A number of systems are available for removing the wool fat by extraction with a volatile organic solvent. Such processes do not remove the suint, and they are followed by a mild warm scour The wool fat and suint are thus obtained separately, and the fat and potassium carbonate can be readily recovered for sale. The advantages of the system are stated to be that a higher weight of clean fibre is obtained, that no matting, felting or fibre breakage occurs, and that there is no danger of alkali damage. On the other hand, the plant is expensive, and when the solvent used is inflammable there is risk of fire. The process is used on a considerable scale in America, employing light mineral oil, but is less used in England.

Various types of apparatus have been designed for carrying out the process. In some forms of plant the extraction takes place in a centrifugal machine, and the residual solvent is driven out with water or is dried off with an inert gas. Alternatively extraction takes place in a series of tanks operated on the counter-current principle. Continuous systems have also been designed, in one of which the wool is carried through a succession of tanks between two endless bands of wire gauze

If wool is extracted exhaustively with a solvent it becomes harsh, brittle and inelastic, but this can be avoided by giving it a final wash in a bath of solvent containing a small proportion of a suitable fat or oil

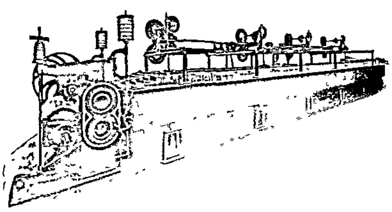

FIG. 12.

Carbonisation of wool.—Scouring does not remove entirely the vegetable matter, consisting of burrs, etc., accumulated by the living animal and present in the raw fleece If left in the wool burrs cause trouble in spinning and weaving and they are not dyed by many wool dyes and so may appear as light places in dyed material. They are removed by the process known as carbonisation, which consists in treating the wool with an acid or an acid salt, drying, and heating. Acids have little effect on wool, but vegetable matter is reduced to a friable pow der, which can be removed by washing or beating.

The commonest carbonising agent is sulphuric acid ; it is convenient, cheap, and acts at a comparatively low temperature. The wool is impregnated with a 2–5% solution at or near the boil, and squeezed or hydro extracted to remove the bulk of the liquor The moist wool is then dried at 60°–70°, and heated for a short time at a higher temperature, but usually not above 105°. Sulphuric acid may be replaced by magnesium or aluminium chlorides, or by hydrogen chloride After carbonisation the vegetable matter is removed by beating or washing. It is advisable to remove the acid by a wash with sodium carbonate, or the material may dye unevenly.

Loose wool is usually carbonised after scouring. If carbonised before scouring the suint should be washed out or it will neutralise the acid. For very burry wool it is recommended to carbonise in the grease, as this acts as a protection to the wool. Cloth may be impregnated and squeezed or centrifuged in the rope form, and then opened out for drying and heating, or it may be treated throughout in the open width

Fig. 12 illustrates a machine made by Messrs. William Whiteley and Sons for steeping

loose wool in acid, and its action is in many respects similar to that of a scouring machine. After steeping, the excess of acid is squeezed out by means of a mangle at the exit end of the machine, and the wool passes to the carbonising apparatus. This may consist of a single chamber, but frequently two chambers are

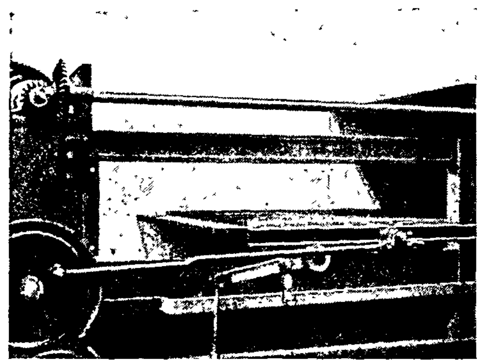

FIG. 13.

preferred. In the latter case the wool is dried in the first chamber, and in the second chamber it is heated to a higher temperature to carbonise the vegetable matter. Fig. 13 shows the construction of a machine made by Messrs. Petrie and McNaught.

The chamber is heated by a current of hot air, and the wool is fed on to the uppermost of a series of shelves, the end of one of which is shown in the illustration. Each shelf consists of alternate fixed and moving bars. The moving bars are raised between the fixed bars by the action of the machine, carry the wool forward a few inches, and then fall again to repeat the operation. The material is thus moved along each shelf in succession and leaves the chamber at the bottom.

Woollen yarn scouring.—Generally yarn is woven from scoured wool, but a further scouring is necessary before certain dyeing operations or before bleaching white, in order to remove the oil with which the wool has been impregnated by the spinner and the dirt and dust accumulated during the mechanical operations. The recent extension of the hosiery industry has increased the frequency of yarn scouring. The amount of oil to be removed is 2–5% for worsted yarns and 10–20% for woollens. The reagents used are the same as for loose wool, namely, soap with the addition of some sodium carbonate, but for worsteds soap alone is often used. The temperature should not be above 60°.

Highly twisted yarn which is liable to curl is first given a permanent set by stretching the hanks tightly on a frame and dipping them for a few minutes in boiling water. The positions of the hanks on the frames are changed several times and the yarn redipped, and it is then allowed to cool in the stretched condition.

Hanks of yarn may be scoured by hand or with the aid of machines. In the first case they are hung on wooden rods so as to dip into the scouring liquor in a rectangular tank, and during 15–20 minutes they are swayed to and fro and are occasionally turned round on the rods. They

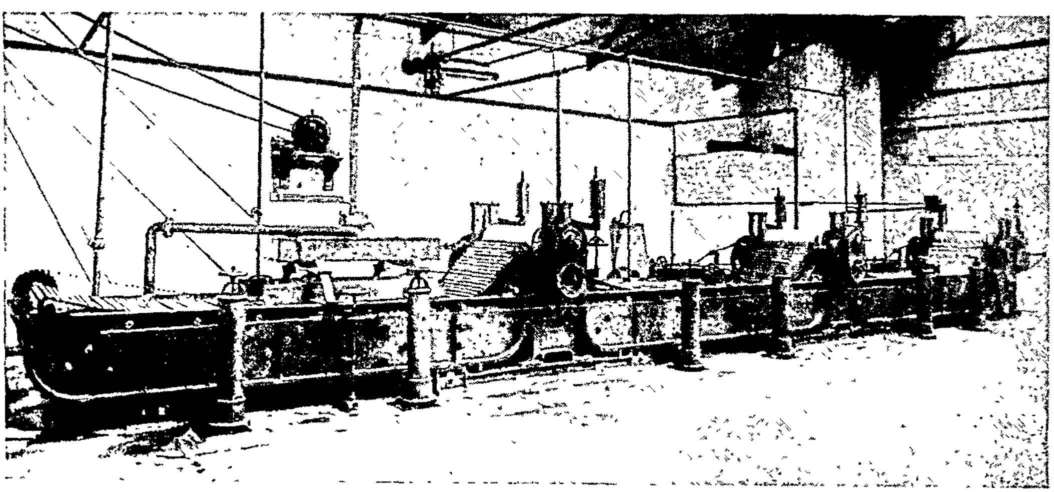

FIG. 14.

are then washed in water in a similar manner. When machines are used the hanks may be stretched between rods supported on the machine or moved on a travelling brattice, or they may be handled as a chain of hanks tied together with string loops. A three-bowl machine of the brattice type, made by Messrs. Petrie and McNaught, is shown in Fig. 14. The hanks are fed on to the brattice in the first bowl, and are sprayed with liquor from an overhead box. When the wool reaches the end of the bowl it is carried between two endless brattices beneath the liquor twice the length of the bowl, and then passes through a powerful mangle into the next bowl.

For worsteds and for good class woollen yarns the oils used in spinning are of animal or vegetable origin with not more than a small proportion of mineral oil, but for yarns of poorer quality mineral oils are more freely used.

The latter are not only unsaponifiable but are difficult to emulsify, and their removal from the wool has presented difficulties. Trotman and Horner [5] find that it is advantageous to add a small proportion of a saponifiable oil and to increase the viscosity of the scouring bath, they recommend the addition of sodium silicate Speakman and Chamberlain [4] show that the chief cause of the difficulty is the high interfacial tension between mineral oil and water together with the strong adhesion of the oil to wool, which increases with the molecular weight of the oil. Efficient scouring requires the presence of 80% of olive oil or of 70% of oleic acid in the mineral oil mixture, but Speakman and Chamberlain find that a much smaller amount of a long chain aliphatic alcohol is sufficient, for example, 6% of oleyl alcohol Such alcohols remain dissolved in the oil during scouring, and their hydroxyl groups greatly reduce the inter facial tension *against water With such an* addition mineral oils can be removed by ordinary scouring methods Sulphonated products are less effective as additions to mineral

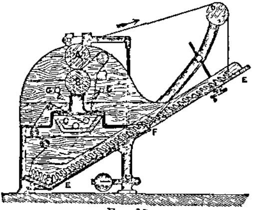

FIG. 15.

oil because they are removed from the oil by the scouring bath. A modern tendency is to avoid the difficulty by making wool oils self-scouring, for example, by sulphonation.

Woollen cloth scouring.—Cloth is usually woven from unscoured yarn and requires scouring to remove the spinning oils and the size added to the warp for weaving. The usual components of sizes are starches, gums, fats and waxes. The scouring agent is soap or soda ash or mixtures of these. When dyed yarns are present care must be taken to avoid undue bleeding; for some dyes sodium carbonate must be avoided and ammonia or ammonium carbonate is used.

The cloth may be handled either in the strand or in the open width. For many woollen cloths the former is preferred, as scouring is then more efficient and a certain amount of felting takes place, which improves the handle. Worsteds and such woollens as are liable to crease are scoured in the open width A machine for this purpose is shown in Fig. 15. It consists of two squeezing rollers A and B, placed above the wooden trough C containing the scouring liquor. The roller D serves to draw the cloth from the squeezing rollers, and causes it to fall in regular folds upon the inclined plane EE. This is covered with corrugated zinc, the grooves of which run longitudinally, in order to reduce the friction of the cloth, and to prevent the latter from moving to either side. The upper part of the inclined plane is hinged at F, so that the inclination of this part can be regulated to suit different qualities of cloth, and to ensure that it always slips down in regular folds without any tendency to fall over or to become blocked. The perforated water pipes GG are for the purpose of washing the cloth after scouring.

Wool bleaching.—Scoured wool has a pale yellow colour and the removal of this is the purpose of the bleaching proper. The required white is obtained by the reducing action of sulphur dioxide either as gas (gas-bleaching or stoving) or in solution (liquid bleaching), or by oxidation with peroxides. Alkaline hypo chlorites and chlorine are inapplicable, as they rapidly attack wool.

Gas bleaching or Stoving—This consists of exposing the scoured and washed woollen material while still moist to the action of sulphur dioxide in a brick chamber Yarn or thick cloth is suspended on poles, the sulphur (6–8% of the weight of wool) contained in an iron pot is ignited, the chamber door closed, and the material is then left exposed to the action of the gas for 6–8 hours or even overnight. Thin cloth is generally passed in a continuous manner through a similar chamber provided with rollers above and below as shown in Fig. 16. The cloth in the open width enters through a narrow slit at one end of the chamber, passes in a zigzag course under and over the rollers to the further end, and then returns and passes out by the same slit. The sulphur dioxide may be produced in the stove itself, but it is preferable to produce it in a separate furnace and lead it into the stove. According to the appearance of the fabric it is passed through the chamber once or several times.

It is difficult or impossible to remove the sulphur dioxide completely from wool by a water wash, but this may be accomplished by a bath of potassium permanganate or of sodium peroxide. The white obtained by this process is not permanent but gradually deteriorates, especially when the wool is washed with soap or other alkaline detergents. To counteract the gradual yellowing the goods are generally tinted blue or violet with suitable dyes.

Liquid bleaching—In this process the material *is immersed in a solution of sulphurous acid, or* of sodium bisulphite and sulphuric acid, or in a solution of sodium bisulphite followed by one of sulphuric acid. A recent patent [2] describes a modified process which uses partly neutralised sulphurous acid, the composition of the bath being $SO_2/NaOH=1/1{\cdot}25$–$1{\cdot}35$. Such baths may be prepared by mixing sodium sulphite and sodium bisulphite, or by adding the requisite amount of an alkali such as sodium hydroxide, carbonate, borate, or phosphate to commercial bisulphite or metabisulphite. A suitable concentration of the bath is 2% of sulphur dioxide, and the p_H is then stated to be 6 8. The wool is immersed in this solution either cold for periods up to 24 hours or more, or

at higher temperatures for shorter times, for example, 2 hours at 50°. The white obtained by this modified process is stated not to deteriorate when the goods are washed with alkaline detergents.

Peroxide bleaching.—Bleaching with either hydrogen or sodium peroxide has recently increased greatly, and it is stated that most white cloth now receives some peroxide treatment. As in cotton bleaching the bath is made slightly alkaline, and the solutions and goods must be kept out of contact with heavy metals. Various alkalis such as ammonia and borax have been suggested, but the best are stated to be sodium metasilicate alone or sodium pyrophosphate together with oxalic acid or sodium oxalate. The temperature should be about 40°, but low-quality goods may require a higher temperature. For the best white the wool should be left acid, and peroxide bleaching is often followed by stoving or by a liquid sulphurous acid bleach.

The white obtained by this process is better than that obtainable by stoving and is permanent. The highest whites are, however, obtained only at some sacrifice of strength, and excessive bleaching results in a harsh handle. The process is used especially for high-class goods and for hosiery.

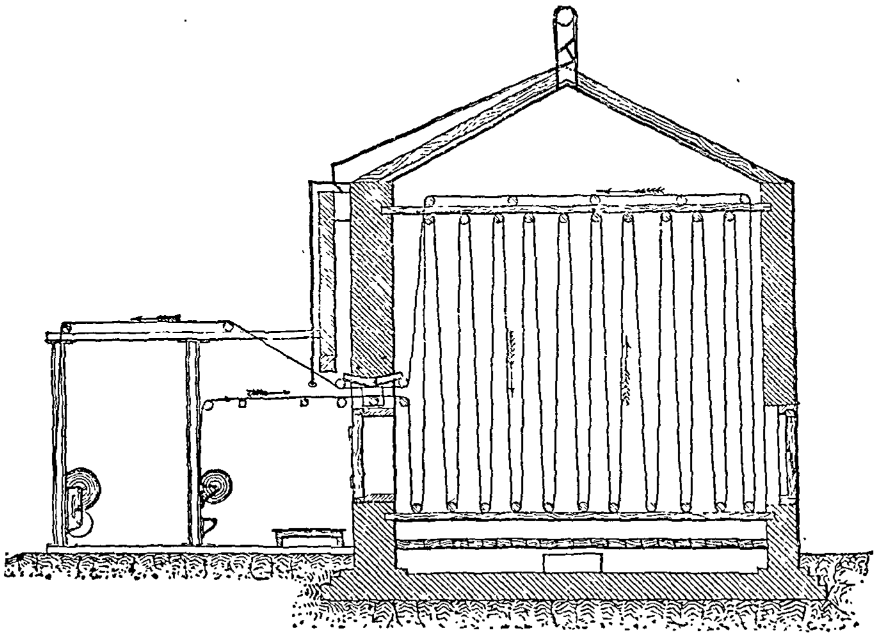

FIG. 16.

SILK.

Composition of Raw Silk.—Raw silk consists of a double filament of fibroin covered with a layer of silk gum; the gum surrounds each of the filaments of fibroin and cements the two together. Silk gum consists chiefly of sericin, but contains also small amounts of fats, of mineral substances, and of yellow colouring matters, chiefly xanthophyll. Fibroin and sericin are both proteins, but they differ in their content of various amino-acids and in their physical properties. Neither is attacked by cold water, but when heated with water under pressure sericin is dissolved and fibroin also is attacked. They are hydrolysed much more readily by alkalis than by acids. Sericin is attacked more readily by alkalis than is fibroin, and swells and dissolves when heated with even such a mild alkali as a soap solution.

Silk degumming.—Raw silk is harsh, stiff and lustreless, but when the external layer of gum is removed it becomes soft and lustrous and the dyeing properties are improved. The substances to be removed include not only sericin, but also the natural fats and colouring matters contained in the gum and any fats and tinting colours that may have been added by the throwster in preceding operations. Care must be taken that the fibroin filaments are not attacked, or the lustre and strength of the silk will be impaired.

Generally silk is degummed as hanks of yarn. Degumming as cloth has the advantages that the gum protects the silk during the weaving process, and that dirt accumulated in this process is removed with the gum. It is adopted generally when silk is woven in conjunction with other fibres and for *crêpe de Chine*. Broken or tangled filaments that are unsuitable for thrown silk are utilised by spinning, and for such material degumming may precede spinning.

Much the most usual degumming agent is aqueous soap solution at or near the boil. The water used must be free from calcium or magnesium, and if either of these is present in the silk it should be washed with hydrochloric acid before degumming. The soap used must be soluble and free from excess alkali. Oleic acid soaps are preferred, and it is stated that soaps of unsaturated fatty acids leave the silk

in a more lustrous condition than do those of the saturated fatty acids. Potassium soaps are recommended in preference to sodium soaps, but they have the disadvantage of greater cost. The p_H of the soap degumming bath is important. If it is above 10.5 the fibroin is weakened, whilst if it is below 10.0 degumming is too slow. During the operation the p_H falls, but the soap bath can be used for the treatment of further batches of silk if the p_H is first re-adjusted by the addition of alkali.

In carrying out the operation the silk hanks are hung on wooden rods in a 1–2% soap solution. This is heated with steam to the boil, and degumming should then be complete in one to two hours. In some processes the silk is treated in a second or even in a third bath. The baths may then be worked on the counter current principle, and the individual treatments may be shorter. During the boil the hanks are moved round on the rods a few times to ensure thorough treatment. Great care is necessary in the mechanical handling of the silk as the filaments are liable to become disintegrated in places to fine fibrils, and the small tangled masses of fibrils, known as flocons, show as light spots in the dyed material. The used soap solution, containing a large proportion of sericin, is known as "boiled off liquor." It is valuable as a restrainer to promote the level dyeing of silk, because it forms stable emulsions in acid solutions. When boiling is finished the silk is washed in a very dilute solution of soda ash or of soda ash and soap, and then in soft water, and finally it is brightened in dilute formic acid. Cloth is singed on both faces before degumming.

Silk which is resistant to degumming, either on account of the thickness of the layer of gum or because the filaments have been tightly twisted, may be sewn in bags and given a further boil with soap, the so called "white boil."

With the object of reducing the number of flocons by diminishing the movement of the silk, this is sometimes placed in a box with a perforated bottom which is fixed over the boiling soap bath. The silk is thus exposed only to the foam, and this method has the added advantage of economising soap. In another procedure the soap solution is sprayed over the silk.

The cost of the soap used in degumming is considerable and many other alkalis, such as sodium hydroxide, carbonate, silicate or phosphate have been suggested as alternatives. They are stated to have the disadvantages of being more liable to attack the fibroin and thus spoil the lustre, of removing the fats and waxes less completely, and of leaving the silk in an inferior condition. Degumming can also be achieved with acids or with various enzyme preparations, but these are less efficient than soap and they do not remove fatty substances.

Silk bleaching.—The colouring matters of raw silk are chiefly in the gum, and after complete degumming the fibre is nearly white. Further bleaching is, however, necessary if the silk is to be marketed white or is to be dyed in pale shades. Bleaching may be effected by exposing the silk while still moist to the fumes from burning sulphur as described for wool, but the use of peroxides is now preferred. Stoving with sulphur has the same disadvantage as with wool, namely, that the white so obtained is not permanent. To compensate for the gradual yellowing, silk bleached by this process is tinted in pale blue or violet shades.

Bleaching baths of hydrogen or sodium peroxide must be made slightly alkaline as for other fibres. For this purpose the addition of ammonia, soap, sodium silicate, or sodium silicate and soap is recommended. Hydrogen peroxide is diluted to about 2 volumes strength with the addition of the alkali, and, after adding the silk, is heated to 50°; treatment lasts for 8–10 hours or overnight. Silk is sometimes stoved before treatment with peroxides.

Slightly acid perborate is stated to be a good bleaching agent, but to require careful control.

Special processes.—The process of degumming described above results in a loss of weight of 20–30% according to the type of silk, and the consumption of soap adds considerably to the cost of the bleached material. Processes are therefore in use which aim either at conserving weight or at economising soap, and the latter are used especially for inferior qualities of silk, for which expensive degumming processes would be less justified.

(*a*) *Spun Silk and Waste Silk.*—In degumming waste silk for subsequent spinning the soap is replaced, either partly or wholly, by soda ash. Thus waste silk is boiled with a soda ash solution (about 0.2%) for an hour, and, when light shades are to be dyed, this treatment is followed by a boil with a relatively small amount of soap.

(*b*) *Souple Silk.*—The term "souple" is applied to silk which has been so treated as to soften the gum without removing the whole of it. The silk is soaped at 40° for ¾ hour, and the resultant loss of weight is only 5–10%. Subsequent bleaching is more difficult than after complete degumming, as the gum has to be bleached in addition to the fibroin. Sometimes, therefore, souple silk is given a preliminary bleach in very dilute *aqua regia*, or in a mixture of sulphurous and sulphuric acids. The bleached silk is soupled by boiling, for example, with a solution containing cream of tartar, sulphuric acid, and sulphurous acid, and it is then washed and dried. In addition to the conservation of weight this process has the advantage that the presence of gum facilitates subsequent weighting.

(*c*) *Écru Silk.*—This is raw silk which has been washed with a tepid soap solution to remove dirt. Such silk is unsuitable for bleaching or for dyeing in colours, and can be used only undyed or dyed black. The loss of weight is 2–3%, and even this loss is avoided if the silk is first treated with formaldehyde.

(*d*) *Tussah Silk.*—Wild silks, such as Tussah, are more strongly coloured and more resistant to degumming and bleaching treatments than are the cultivated varieties. More strongly alkaline baths are used for degumming, and Tussah silk generally requires to be boiled in at least two baths of soda ash and soap. Even when completely degummed it is difficult to bleach, and it is used frequently in its natural shade. It cannot be bleached with sulphur

dioxide, and the best treatment is a boiling peroxide bath.

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A. G.

BLEACHING POWDER. A white powder prepared by the action of chlorine on slaked lime; the composition is expressed by the formula $CaCl(OCl),H_2O$ (*v.* BLEACHING).

BLENAL. Trade name for santalyl carbonate. Inodorous, substitute for santalol.

BLENDE, from Ger. *Blenden*, to dazzle. Native zinc sulphide. It usually contains iron, which gives it a black colour, whence the name Black Jack applied to it. An important ore of zinc. The sulphur it contains is occasionally utilised in the manufacture of sulphuric acid. (For descriptions of burners for this purpose *see* J.S.C.I. 1884, 3, 631; 1885, 4, 54).

BLEU CELESTE *v.* BLUE CERULEAN.

BLEU DE SAXE, *smalt, bleu d'azur*, a silicate of cobalt and potassium.

BLIND COAL. A Scotch term for anthracite.

BLISTER STEEL. Bar iron is surrounded with charcoal and heated for about 7 days. The product is known as " blister steel."

BLOEDITE. A hydrated double sulphate of magnesium and sodium,

$$Na_2Mg(SO_4)_2,4H_2O,$$

forming water-clear monoclinic crystals, often of large size and beautifully developed. They are found in the salt mines of Stassfurt and in Poland, and in the Punjab Salt Range, India. Crystals 16½ cm. in length have been found in the black mud beneath a crust of sodium sulphate on Soda Lake, San Luis Obispo Co., California. Simonyite and astrakanite (from salt lakes near Astrakan) are synonyms.

L. J. S.

BLOMSTRANDINE. A rare-earth mineral consisting of a titano-columbate of yttrium-metals, thorium, uranium, etc., occurring as orthorhombic crystals in pegmatite veins at several localities in southern Norway. The large crystals of tabular habit are found in the felspar quarries, and those from the island of Hitterö are well known in collections. They are brown on the surface, but on a fresh conchoidal fracture the colour is black with a bright pitchy lustre. The mineral is optically isotropic, owing to alteration by hydration. Sp.gr. 4·82–4·93. These crystals were provisionally referred by W. C. Brögger in 1879 to æschynite (*q.v.*), an allied species differing mainly in containing cerium-metals in place of yttrium-metals. More recently, Brögger (" Die Mineralien der südnorwegischen Granit-Pegmatitgänge," Videnskabs-Selskabets Skrifter, Kristiania, 1906) has given a detailed description of this material, and he gives several other Norwegian localities for the mineral, namely, near Arendal and in Sætersdal. He interprets the complex composition as an isomorphous mixture in varying proportions of a metacolumbate with a metatitanate; and for another member of the same series from the tin gravels of Swaziland, Transvaal, shown by G. T. Prior's analysis (1899) to contain more columbium with less titanium, he proposed the name *priorite*. These isomorphous minerals, blomstrandine and priorite, are respectively dimorphous with polycrase and euxenite; the four minerals euxenite-polycrase and priorite-blomstrandine thus forming an isodimorphous series.

The name blomstrandine is not to be confused with the earlier name *blomstrandite* (of G. Lindström, 1874), which was applied to an uncrystallised hydrated titano-columbate and tantalate of uranium with some calcium and iron, from a felspar quarry at Nohl, in Sweden (*v.* BETAFITE).

L. J. S.

BLOMSTRANDITE *v.* BETAFITE and BLOMSTRANDINE.

BLOOD is a richly albuminous fluid which holds in suspension large numbers of corpuscles. The fluid medium in which the corpuscles float is called the plasma. In round figures, the plasma contains about 10% of solids, of which proteins comprise 8, extractives 1, and inorganic salts (the principal one being sodium chloride) the remaining 1. The proteins are all coagulable by heat, and are named serum albumin, serum globulin, and fibrinogen. The last-named is the least abundant (0·4%), but confers upon the blood its characteristic power to clot or coagulate when it is shed. When shed, the blood rapidly becomes viscous, and then sets into a jelly; the jelly contracts and squeezes out of the clot a straw-coloured fluid called serum, in which the shrunken clot then floats. The formation of threads of a solid protein called fibrin from fibrinogen is the essential act in coagulation; this with the corpuscles it entangles constitutes the clot, and serum is plasma *minus* the fibrin which it yields. The following scheme shows at a glance the relationships of the constituents of the blood:

$$\text{Blood}\begin{cases}\text{plasma}\begin{cases}\text{serum}\\ \text{fibrin}\end{cases}\\ \text{corpuscles}\end{cases}\Big\}\text{clot.}$$

In round figures, the blood contains 60–65% of plasma, and 35–40% of corpuscles. The corpuscles are of three kinds, the red corpuscles or erythrocytes, the white or colourless corpuscles or leucocytes, and some very small particles, also colourless, which are called the blood-platelets.

The subject of blood clotting is dealt with in a later section of this article (*q.v.*).

The white or colourless corpuscles are typical nucleated animal cells which have been differentiated into varieties by their staining reactions, the number of their nuclei, and their seat of origin (lymphoid tissue, and red bone marrow). Their most important property is their power of amœboid movement, by which they ingest and subsequently digest foreign particles. They act

in this way as scavengers (phagocytes), and thus confer protection against pathogenic organisms (bacteria, etc).

The red corpuscles are much more numerous than the white, averaging in man 5,000,000 per cubic millimetre, or 400–500 red to each white corpuscle. It is these which give the red colour to the blood They vary in size and structure in different groups of the vertebrates. In mammals, they are biconcave (except in the camel tribe, where they are biconvex), non nucleated discs, in man 7 8μ in diameter, during fœtal life nucleated red corpuscles are, however, found In birds, reptiles, amphibia, and fishes, they are biconvex oval discs with a nucleus , they are largest among the amphibians Their most important and abundant constituent is the pigment hæmoglobin In invertebrates this respiratory pigment is usually absent, and when present is, with few exceptions, in solution in the plasma and not in special corpuscles In other invertebrates its place is taken by other respiratory pigments, for instance, by the green pigment which contains iron and is called chlorocruorin (in certain worms), or by the blue pigment which contains copper and is termed hæmocyanin (in certain crustaceans and molluscs). The vast majority of invertebrates have colourless blood containing only colourless corpuscles

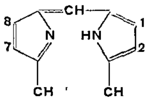
Hæmoglobin and the Porphyrins.—Hæmoglobin contains 0 4% of iron , it and certain of its derivatives give characteristic absorption spectra which form one of the best tests for blood. It is termed a conjugated protein, consisting of a protein (globin) in combination with the iron containing material termed hæmatin. The molecular weight of hæmoglobin has been determined by independent methods which have yielded remarkably concordant results. Thus Adair (Proc. Roy. Soc 1925, 98 [B], 523) deduced from osmotic pressure measurements a molecular weight of 67,000 ; Svedberg (Z. physikal. Chem. 1927, 127, 51), from experiments on the rate of sedimentation of hæmoglobin molecules in the ultra centrifuge, arrived at a molecular weight of 68,000 , Northrop and Anson (J. Gen. Physiol 1929, 12, 543), with the help of the Einstein equation and a direct measurement of the diffusion coefficient of carbon monoxide-hæmoglobin, assign to the protein a molecular weight of 68,500±1,000

A molecule of this order of magnitude is required by the currently accepted theories of the constitution of hæmoglobin which appears to consist of four hæmochromogen units each comprised of hæmatin in association with globin, a simple basic protein. Hæmatin is an iron compound of protoporphyrin. The latter, which contains two unsaturated side chains, readily hydrates to yield hæmatoporphyrin on being liberated from hæmoglobin by the action of acids. By boiling dried blood with a little sodium chloride and glacial acetic acid, the characteristic brown crystals of hæmatin hydrochloride or hæmin are readily obtained, and this is a very convenient chemical test for blood ; it can be performed quite readily on a microscope slide. Reduced hæmatin may be prepared from hæmin by the action of sodium hyposulphite and alkali, and this, in contact with denatured globin, yields a hæmochromogen with a molecular weight of about 17,000. In contact with natural globin hæmatin yields reduced hæmoglobin.

By treatment with acid, as already stated, an iron free derivative of hæmatin is obtained called hæmatoporphyrin, and in the body certain iron-free derivatives somewhat similar to hæmatoporphyrin are formed ; these constitute the pigments of the bile. By the reduction of hæmatoporphyrin, hæmopyrrol (a mixture of pyrrol derivatives) is obtained, and the same substances are obtained also from phylloporphyrin and ætioporphyrin, derivatives of chlorophyll ; this is an interesting fact, as it indicates a near relationship between the principal pigments of the animal and vegetable worlds

For hæmin the following formula may be regarded as established, $C_{34}H_{32}O_4N_4FeCl$. It is supported by the synthetic achievements of H. Fischer and Ziele (Annalen, 1929, 468, 98) who have obtained hæmatoporphyrin, protoporphyrin, and hæmin, using as starting material deuteroporphyrin. The latter is obtained by fermenting fresh ox-blood spontaneously, or with yeast, in an alkaline medium. Deuteroporphyrin was converted to its C diacetyl derivative, and the latter when boiled with potassium hydroxide in absolute alcohol yielded hæmatoporphyrin. At 105° in a high vacuum the free hæmatoporphyrin was converted almost quantitatively into protoporphyrin identical with that derived from the hæmoglobin of blood The action of hydrogen iodide in glacial acetic acid on the synthetic hæmatoporphyrin hydrochloride yielded mesoporphyrin, the fully hydrogenated homologue of protoporphyrin, whilst from the synthetic preparation of the latter, hæmin has been obtained by the standard methods.

The inter-relationships of these porphyrins are shown by the skeleton structural formula given below, whilst the probable positions of the substituent side chains in the porphyrins mentioned above, and also in ætioporphyrin obtainable from chlorophyll, are indicated in the appended table, the numbers 1–8 corresponding to the positions marked in the skeleton formula :



Hæmoglobin is crystallisable. From different animal species distinctive crystalline forms of

THE SUBSTITUENT SIDE-CHAINS OF THE PORPHYRINS.

	1	2	3	4	5	6	7	8
Ætioporphyrin .	C_2H_5	CH_3	CH_3	C_2H_5	CH_3	C_2H_5	C_2H_5	CH_3
Deuteroporphyrin	H	CH_3	CH_3	H	CH_3	$CH_2.CH_2.COOH$	$CH_2.CH_2.COOH$	CH_3
Protoporphyrin .	$CH:CH_2$	CH_3	CH_3	$CH:CH_2$	CH_3	$CH_2.CH_2.COOH$	$CH_2.CH_2.COOH$	CH_3
Mesoporphyrin .	C_2H_5	CH_3	CH_3	C_2H_5	CH_3	$CH_2.CH_2.COOH$	$CH_2.CH_2.COOH$	CH_3
Hæmatoporphyrin	$CH(OH)CH_3$	CH_3	CH_3	$CH(OH)CH_3$	CH_3	$CH_2.CH_2.COOH$	$CH_2.CH_2.COOH$	CH_3

hæmoglobin have been obtained. In this connection the detailed studies of Reichert and Brown should be consulted ("The Crystallography of Hemoglobin," Publication No. 116, Carnegie Inst. of Washington, 1909).

Physiology of Blood.—During life the blood is in constant movement (circulation), and it is owing to this circumstance that it supplies the tissues with both nutriment and oxygen. The products of protein and carbohydrate digestion pass directly from the alimentary canal into the blood-vessels; the fat reaches the blood indirectly by the lymph-stream. The blood, however, does not, except in the spleen, actually bathe the tissue elements; the middleman between blood and tissues is a fluid called lymph, which exudes from the blood through the thin walls of the capillary blood-vessels. The lymph thus supplies the tissues with material for their repair or for storage; it also removes from the tissues the waste products of their activity; it is collected by lymphatic vessels which converge to the main lymphatic channel called the thoracic duct. This opens into the large veins near to their entrance into the heart, and thus the lymph is returned to the blood, and the waste products are then conveyed to the various organs (lungs, kidneys, skin) by which they are discharged from the body.

The function of blood as an oxygen carrier is dependent on the presence of hæmoglobin. Oxygen passes by diffusion into the blood of the lungs, where it comes into contact with the pigment, and with which it forms a loose compound called oxyhæmoglobin; this bright-red arterial or oxygenated blood passes to the heart, and is thence propelled through the arteries all over the body; in the tissues, where the oxygen tension is very low, oxyhæmoglobin is dissociated, and the oxygen passes into the plasma, and again reaches the actual tissue elements *via* the lymph. The reduction of oxyhæmoglobin changes the colour of the blood to the darker tint which it has in the veins, by which vessels it is carried back to the heart and sent to the lungs for a fresh supply of oxygen. The venous blood is also rich in carbon dioxide, which finds an exit from the blood in the lungs into the expired air. It is probable that a small proportion of this carbon dioxide is carried in direct combination with hæmoglobin and other proteins, but the great bulk of the gas is carried in the form of carbonates in the blood-plasma.

The amount of respiratory oxygen carried by the blood pigment is 1·34% oxygen per gram of hæmoglobin. This can be replaced by equivalent amounts of such gases as carbon monoxide or nitric oxide. These compounds are more stable than oxyhæmoglobin, and the gas is not removable by the tissues; hence in coal-gas or exhaust-fume poisoning the colour of the blood is equally bright in arteries and veins, and the cause of death is oxygen starvation.

Technical and Commercial Uses of Blood.—Passing now to the technical and commercial aspect of the case, the uses of the blood come mainly under four headings: (1) as food; (2) as manure; (3) as a clarifying agent; and (4) as a drug.

(1) *As Food.*—Blood as such is only used as food by savages, and attempts have been made to utilise dried defibrinated blood as a commercial food product without any great success. It, however, forms an important constituent of certain articles of diet, of which black pudding and the German *Blutwurst* (blood sausage) are the best known. In the preparation of these pig's blood is most commonly employed, and they are of high nutritive value. (For the composition of various kinds of Blutwurst, *see* König, Chemie d. menschl. Nahrungs und Genussmittel, Berlin, 1904, 525; Pott. Handb. d. Tier-Ernährung, iii, 513, 1909; E. Schmidt, Lehrb. d. pharm. Chem. ii, 2, 1833, 1901.)

(2) *As Manure.*—Dried blood, the so-called blood-meal (*Blutmehl*), is extensively used as manure, and may be placed directly on the land, or, more frequently, is mixed with superphosphates. It is a brown powder with a glue-like smell, and must be kept in dry places to avoid putrefaction. It is valuable on account of its high percentage of nitrogen (11·8%) and of phosphorus (1·2%). Numerous patent manures contain a certain proportion of blood. (For details, *see* König, *l.c.* 496; Merck's "Waren-Lexicon," 5th ed., art. Blut.)

(3) *As a Clarifying Agent.*—Blood is employed in the same way as are milk, gelatin, and albumin, as a clarifying agent for wines, syrups, and similar liquids, in the proportion of 150–200 c.c. of blood per litre. The clearing action is due to the proteins present, but used in this way there is considerable danger of infection, as also is the case for milk. Dried blood or the dried blood-albumin is therefore preferable. Blood-albumin is prepared from the serum drained off from the clot; the product is really dried serum, as the proteins are mixed with the other constituents of that fluid, and the word "albumin" is used as synonymous with "protein" and not in the correct chemical sense.

It has the advantage of being considerably cheaper than egg-albumin, for the total blood of an ox will yield 750–800 g. of the dried product, a good-sized calf will yield 340–400 g., and a sheep about 200 g. (*see* Merck, *l c.*, art. Blutalbumin).

(4) *The Therapeutic Uses of Blood and Serum* — The high nutritive value of blood makes it a valuable drug in the treatment of anæmia, and certain patent medicines sold under the name of *hæmatogen* consist very largely of blood mixed with suitable flavouring and preservative agents A still larger practical use of blood products (serum therapy) has been the outcome of work on immunity, in which the names of *Richet, Ehrlich, Behring, and Roux* may be mentioned as those of pioneers. In connection with these and similar problems reference may be made to "Vaccine and Serum Therapy" by Fleming and Petrie, 1934 (Churchill, London), and to "Hæmatology," by Piney, 1930 (Churchill, London).

Miscellaneous Uses of Blood.—Blood is, or has been, employed in a number of industrial processes, *e g* as a medium for paints (Johnson, B P. 82, 1883), in the preparation of adhesive cements, as a precipitant of sewage in the alum, blood, and clay process; and in the manufacture of pure animal charcoal.

Tests for Blood.—It is often necessary, in medico legal practice, to be able to identify *blood stains on garments and instruments* If the blood is fresh, a microscopic investigation reveals the presence of corpuscles, and an aqueous extract will show the typical absorption bands of hæmoglobin with the spectroscope. The best chemical test is the formation of hæmin crystals already described, and is given by quite small quantities of blood, even if it is old and dry. When the blood is dry, and small quantities only are present, the most delicate spectroscopic test consists in dissolving it in dilute potash with the aid of heat, and then adding a drop of a reducing agent such as ammonium sulphide; the two absorption bands of reduced hæmatin are then seen, one about half-way between the D and E lines, and the other just on the blue side of the E line.

Human blood can only be distinguished with certainty from the blood of other animals by the so-called "biological reaction." The injection in successive doses of blood of one animal species into another animal of a different species acts as an *antigen*, and causes the development of a specific *precipitin* in the blood of the injected animal. The addition of a trace of blood of the first animal species to the serum of the injected animal causes a precipitate. Such a precipitate does not form except between the blood of the two species of animal used in the experiment. This has been applied to the case of human blood, by taking a rabbit and injecting human blood into it. The serum of this rabbit will then give a precipitate with the blood of man (and to a less extent of the higher apes), and with the blood of no other species of animal. The test is extraordinarily delicate, and will detect human blood that has been dried for months, and even when it is mixed with the blood of other animals.

J. P.

Blood Coagulation.

When blood leaves the blood vessels it clots within a few minutes, the clot formed assisting in preventing further hæmorrhage. Clotting, therefore, is an important protective mechanism against excessive drainage of blood from the organism. In hæmophilia there exists a congenital deficiency in the coagulative power of the blood. A trifling wound, in this disease, leads to persistent bleeding, whilst a larger wound may lead to fatal results.

Coagulation of blood is a complex chemical and physico-chemical process the details of which are not yet fully understood.

Buchanan demonstrated in 1845 that a substance is present in serum which when added to incoagulable exudates of the body causes them to clot. This substance may also be extracted from blood clots. Schmidt in 1872 found that serum contains a substance which converts certain plasma proteins, in presence of calcium, into fibrin. This was termed *thrombin*, and Schmidt showed that it was formed in shed blood from an inactive precursor, prothrombin, which exists normally in the plasma of circulating blood. The fibrin of a blood clot was shown by Hammarsten (1880) to be formed by a reaction between thrombin and *fibrinogen*, a blood protein.

Fibrin is formed in shed blood in the form of fine threads radiating from foci, probably the blood platelets. They form an interlacing network entangling red and white blood cells. It has been observed that the fibrin is deposited in the form of fine crystalline needles, unique conditions peculiar to blood clotting being necessary for the deposition of fibrin in this manner. The blood of invertebrates forms a structureless gel when it clots (Howell).

Stuber and Lang ("*Physiologie und Pathologie d. Blutgerinnung,*" Berlin, 1930) have proposed the theory that blood glycolysis is responsible for clotting, the increased acidity due to lactic acid formation causing precipitation of fibrinogen Wohlisch, however, has pointed out that acid precipitation of fibrinogen is a reversible process, whereas blood clotting is irreversible. Moreover, gradual glycolysis without clotting may take place in a hæmophilic blood. The fundamental process in blood coagulation appears to be a reaction between thrombin and fibrinogen.

Fibrinogen, which gives rise to fibrin, is a globulin which exists in blood to the extent of about 400 mg. in 100 ml. and is probably formed in the liver. It can be prepared by half saturation of blood plasma with sodium chloride. The precipitate of fibrinogen is washed by centrifuging and decantation, with half saturated sodium chloride solution and is dissolved in a weak salt solution. Such a solution forms a clot when it is mixed with a few drops of blood serum (not plasma) owing to the thrombin contained therein. The clotting does not take place if the serum has been heated.

Thrombin shows most of protein reactions, but it is not coagulated by heat. It may be obtained from blood serum by treatment with alcohol, the precipitate being extracted with water which dissolves the thrombin. The pro-

cess is repeated to obtain a purer solution of the substance. The latter has a marked coagulating action on solutions of fibrinogen. Howell (1913) has described a method of separating thrombin from fibrin. Thrombin does not exist in blood plasma ; it is produced at the time of the blood clots.

The nature of the reaction between fibrinogen and thrombin is not yet fully understood. Hammarsten considered thrombin to be a hydrolytic enzyme which hydrolyses fibrinogen to form insoluble fibrin. This view is still maintained by J. Mellanby (Proc. Roy. Soc. 1933 [B], **113**, 93), according to whom thrombin is a proteoclastic enzyme splitting the fibrinogen into fibrin and a soluble serum globulin. He suggests it is an essential factor in blood coagulation *in vivo*. According to Waldschmidt-Leitz and his colleagues (Z. physiol. Chem. 1929, **183**, 39) thrombin is an enzyme related to pancreatic trypsin and may be activated by *thrombokinase*. Fuchs and Zakrzewski (Klin. Woch. Oct. 1934) claim that they have been able to demonstrate an increase in non-protein nitrogen as a result of coagulation, and consider that the result is a demonstration of the hydrolytic action of thrombin. Convincing experimental proof of the alleged hydrolytic action of thrombin is, however, still lacking. The "products of hydrolysis cannot be separated and determined, nor does fibrinogen respond to other hydrolytic agents or enzymes with the formation of a fibrin gel" (Howell).

Del Baere (Biochem. Z. 1932, **246**, 38) explains the deposition of fibrin as due to the electrical adsorption of positively charged thrombin on negatively charged fibrinogen.

Thrombin is derived from prothrombin, a protein which normally exists in the plasma of circulating blood, by the action of calcium ions and of a substance present in tissue extracts. Morawitz considers its inactivity in normal blood to be due to the lack of the tissue extract activator—thrombokinase. Howell believes that in circulating blood prothrombin is protected by combination with an anticoagulant or inhibiting substance which he has shown to be present in blood. Mellanby, Pickering and Hekma consider that in the normal blood prothrombin is protected because "it exists in a colloidal complex with fibrinogen, serum, globulin and albumin. Exposure to a foreign surface or to the action of tissue extracts causes dissociation of this complex with liberation of prothrombin and subsequent activation." Eagle (J. Gen. Physiol. 1935, **18**, 531) has shown that the amount of thrombin formed in a mixture of prothrombin, calcium ions, and tissue extract varies directly with the amount of prothrombin and not with the other two factors.

Mellanby (Proc. Roy. Soc. 1930, **107** [B], 271) obtains prothrombin by precipitating dilute oxalated plasma with dilute acetic acid at p_H 5·3. The precipitate is treated with dilute calcium bicarbonate solution which dissolves out the prothrombin. This solution is again precipitated with dilute acetic acid and the precipitate centrifuged and dried with acetone. The yield of prothrombin (or prothrombase) is 40 mg. per 100 ml. plasma ; 1 mg. of the preparation, on activation, coagulates 100 ml. plasma in 20 seconds. Morawitz has shown that prothrombin may be obtained from blood platelets, but according to Fuchs and Fischer prothrombin is provided by all or many tissues.

Calcium ions play an important role in the conversion of prothrombin into thrombin but, apparently, are not concerned with the final reaction between thrombin and fibrinogen. Thus clotting will occur when purified thrombin is added to oxalated blood or plasma, or to a pure solution of fibrinogen. Thrombin is not a calcium compound because the activation of prothrombin into thrombin may occur in the absence of calcium, *e.g.* by alcohol or chloroform. Traces of calcium appear to accelerate considerably the normally slow change of prothrombin into thrombin, but agreement on this point has not been universally reached. Strontium, and to a far smaller extent, barium and magnesium, will catalyse the conversion of prothrombin into thrombin.

An additional factor in the activation of prothrombin is present in the form of thrombokinase which is supplied by tissue elements and especially by blood platelets. According to Howell this tissue factor removes an inhibitor from combination with prothrombin ; according to Pickering the tissue factor causes dissociation of a complex of prothrombin, fibrinogen and tissue proteins.

This tissue activator is supposed to resemble lecithin, and it may be extracted from tissues by alcohol and ether ; it is then thermostable. Brain cephalin, which may be identical with, or nearly related to, thrombokinase, according to Howell, is particularly potent as an activator. Its potency is lost when the cephalin is allowed to stand in air, and is retained when the cephalin is kept *in vacuo*. Lecithin, free from cephalin, has no effect on coagulation. Fischer and Hecht (Biochem. Z. 1934, **269**, 115) claim that the purer the preparation of cephalin the less is its effect on coagulation. Charles, Fischer, and Scott (Trans. Roy. Soc. Canada, 1934, **28**, V, 49) have isolated from lungs a thrombokinase, which, whilst a lipoid related to fatty acids, is not cephalin.

Howell considers that blood contains traces of some compound, similar to the hirudin of leeches and other blood-sucking animals, which is an anticoagulant. Howell and Holt (Amer. J. Physiol. 1918, **47**, 328) have given the name *heparin* to an anticoagulant from dog's liver. It has no inhibitory effect on the action of purified thrombin on fibrinogen but it inhibits the conversion of prothrombin into thrombin. It is free from phosphorus and nitrogen and appears to be a glycuronic acid derivative. Chargaff, Bancroft, and Stanley Brown (J. Biol. Chem. 1936, **115**, 155) conclude from a recent study of anticoagulants that such substances "must be water soluble, of high molecular weight and must contain combined sulphuric acid or possibly other acid groups of similar strength." They find that an active anticoagulant is galactan-sulphuric acid ester isolated from an alga, *Irideae laminarioides*.

Morawitz's Theory of Blood Coagulation.—A widely accepted theory of blood coagulation

is that of Morawitz according to which thrombokinase from tissue cells and especially from damaged *blood platelets, acts, in conjunction* with calcium ions, on prothrombin of blood plasma to form thrombin The latter reacts with fibrinogen to produce fibrin

Thus we have

(1) Prothrombin + Ca + Thrombokinase = Thrombin

(2) Thrombin + Fibrinogen = Fibrin

Howell's Theory of Blood Coagulation — Howell believes that prothrombin can be converted to thrombin by the action of Ca'' alone The thrombokinase, or tissue activator, acts not as a kinase but as a substance neutralising a normal inhibitor of prothrombin This inhibitor (possibly heparin) when combined with prothrombin, prevents the latter being converted by calcium ions into thrombin The shedding of blood and consequent destruction of blood platelets furnish the tissue activator which combines with the inhibitor and thus liberates free prothrombin (*see also* Chargaff *et al*, J Biol Chem 1936 115, 237)

Thus we have

(1) *Prothrombin heparin + tissue factor (cephalin ?)* = Prothrombin
(2) Prothrombin + Ca'' = Thrombin
(3) Thrombin + Fibrinogen = Fibrin

For a discussion of these and other theories of blood coagulation (*e g* those of Bordet, Pickering, Fuchs, and Fischer) each of which has its distinctive features, the reader is referred to Howell (Physiol Rev 1935, 15, 435) For fuller information on the subject the reader is referred to the above article and also to Wohlisch (Ergeb d Physiol. 1929, 28, 443), Fuchs (Ergeb d Enzymforschung, 1933, 2, 282), and Zung (Traite d Physiol (Roger et Binet), 1934, 7, 189) J. H. Q

Anticoagulants

Defibrination.—This process of preventing coagulation of blood is usually carried out when mineral analyses are to be made on the blood serum and when the introduction of extraneous substances is undesirable. It is carried out by stirring the blood in a tube with a glass rod, the clot adhering to the rod. Care should be taken to prevent the rod coming into contact with the sides of the vessel as this may break up the cells, causing hæmolysis Defibrination should be carried out as far as possible anærobically, as otherwise loss of CO_2 and absorption of O_2 may occur (*see* Eisenman, Method for Anærobic Defibrination of Blood, J. Biol. Chem. 1925, 71, 607).

Oxalate and Citrate —These substances appear to depend on their combination with blood calcium for their powers of preventing blood coagulation. For analytical purposes citrates *should be avoided as they interfere* with uric acid determination, protein precipitation, and cause disturbances in reaction and cell volume Oxalates (K, Na, or NH_4 salts) are effective anticoagulants *in a concentration of 0 1 to 0 2%* They are most favoured in analytical work as they have little influence on p_H and on the CO_2 absorbing power of the blood. For details of the use of oxalate, *see* Peters and Van Slyke ("Quantitative Clinical Chemistry," 1932. II, 61), and Magath and Hurn (Amer. J. Clin. Path. 1935, V, 548)

Hirudin —This active principle of the secretion of the buccal glands of leeches is now rarely used as an anticoagulant and has been replaced by heparin

Heparin —This anticoagulant was obtained from dog's liver by Howell and Holt (*l c.*) and is to be found in the liver, lungs and muscle. It has no effect on the reaction between purified thrombin and fibrinogen, but it inhibits the conversion of prothrombin into thrombin. It prevents coagulation at a concentration as low as 1 mg. per 100 ml. It appears to be a glycuronic acid derivative.

Venom of the viper (*Viperinæ* and *Crotalinæ*) contains thrombin, which if introduced into the body will cause intra vascular clotting. This coagulant action of viperine venom has been used in the treatment of hæmophilia. The Indian *daboia* venom (*Vipera russellii*) has been found to be by far the most powerful coagulant agent against hæmorrhage. Experimentally, one drop of Russel's viper venom in a concentration of 1/1,000, when added to 10 drops of hæmophilic blood, clotted it in 17 seconds, whereas the blood from the same *patient clotted spontaneously in 35 minutes.* The effect of the venom may be observed even in dilutions of 1 in 10^{18}. For further details of the therapeutic effects of venoms the reader *is referred to Chopra and Chowhan* (Snake Venoms in Pharmacology and Therapeutics, Indian Medical Gazette, 1935, 70, 445).

When an animal survives for an hour or two after *injection of the viper venom* the blood is incoagulable (Taylor, Mallock, and Ahuja, Indian J. Med. Res 1935, 23, 131). Coagulability returns to normal gradually in animals which survive. "The intravenous coagulation and incoagulability of the blood are manifestations of action of the venoms which differ only in degree and rapidity. Rapid action of the venom may produce massive clotting of the blood *in vivo*, while slower action produces invisible coagulation, probably with fine deposition of fibrin in the walls of the blood vessels, the blood being defibrinated and in consequence incoagulable."

Antivenenes (*antivenom sera*) will bring about a neutralisation of the coagulant action of the venom, the homologous antivenene being the most effective. Taylor *et al.* (*l c.*) report experiments where the addition of neutralised venom (venom + homologous antivenene) at a concentration of 1 in 10^4 to 1 in 5×10^6 prevented the coagulation of sheep's blood. They state that the coagulant actions of *daboia* and *Echis* venoms are neutralised by their respective antivenenes. *Daboia* antivenene does not neutralise the coagulant action of *Echis* venom nor does *Echis* antivenene neutralise that of *daboia* venom, specificity of action being clearly observed J. H. Q

BLOOD CEMENTS *v.* Adhesives *and* Adhesive Action.

BLOODSTONE. A popular name for the mineral heliotrope, a variety of chalcedony (SiO_2), showing bright-red spots on a dark-green ground. It is used for the engraving of ring-stones and seals.

The same name has also been used for hæmatite, (Fe_2O_3), being a translation of *αἱματίτης*, so called because the colour of the powdered mineral is like that of dried blood.

L. J. S.

BLOOM. A term given to a mass of iron after it leaves the puddling furnace.

BLOWN OILS. Thickened oils, soluble castor oils, are prepared by blowing air through vegetable *semi*-drying oils, blubber oils, or liquid waxes whilst these are stirred and heated to temperatures varying from 70° to 115°. The products are denser and more viscous than the raw materials and are miscible with mineral oils. These mixtures are used as lubricants. The blown oil from linseed oil which sets by further oxidation to an insoluble solid, *linoxyn*, is employed as the agglutinant in the manufacture of linoleum.

BLUE ASHES *v.* BLUE, MOUNTAIN.

BLUE, BERLIN *v.* BLUE, PRUSSIAN.

BLUE CERULEAN. *Cœruleum, Cœlinblau, bleu celeste*, Cobalt stannate. A greenish-blue pigment.

BLUE, COBALT. *Thénard's blue, Leyden blue, King's blue, cobalt ultramarine, Gahn's ultramarine, azure blue.* A valuable water colour pigment consisting of cobalt aluminate, or a compound of the phosphate or arsenate of cobalt with alumina.

BLUE COPPERAS. *Blue stone* or *blue vitriol*, Copper sulphate.

BLUE CROSS GAS. Diphenyl chloroarsine, $(C_6H_5)_2AsCl$, m.p. 43°, b.p. 333°, yields a very irritant toxic smoke used in gas warfare (*v.* CHEMICAL WARFARE AND DEFENCE).

BLUE 3G (*Cibanone Yellow R*) *v.* ANTHRAQUINONE DYESTUFFS.

BLUE GUM TREE. *Eucalyptus globulus.* A large tree of Tasmania and eastern Australia, its fresh leaves are distilled for the volatile oil, 1 to 3%. A tincture of the leaves is used in the treatment of asthma. The unmixed oil of *E. globulus* is no longer a commercial article, the oil of eucalyptus is obtained by rectifying the distillates from *E. polybractea*, *E. dumosa*, and other species of eucalyptus which yield oils containing a large proportion of cineol, also known as eucalyptol or cajuputol, with some phellandrene. The oil is soluble in 90% alcohol, and contains not less than 70% of cineol. Sp.gr. 0·910 to 0·930, $[a]_D$ +5° to −5°, n_D^{20} 1·458 to 1·470.

BLUE IRON-EARTH. An earthy blue variety of the mineral vivianite, a hydrated ferrous phosphate, $Fe_3P_2O_8,8H_2O$, often found as a blue powder encrusting vegetable remains and bones in bog-iron-ore, peat, and clays.

L. J. S.

BLUE JOHN. A variety of fluorspar found in Derbyshire and valued for making ornamental articles (*v.* CALCIUM).

BLUE LEAD. A term applied to galena by miners to distinguish it from white-lead ore, or carbonate.

BLUE, LIME, and BREMEN BLUE are essentially copper hydroxide, $Cu(OH)_2$, associated with calcium carbonate and copper carbonate respectively, formerly used as pigments.

BLUE, MANGANESE. A blue pigment prepared by igniting at a red heat manganese oxide and barium nitrate with kaolin or with silica.

BLUE, MOUNTAIN. *Blue verditer, chessylite, azurite, blue ashes,* or *Bergblau.* The natural hydroxycarbonate of copper, $2CuCO_3 \cdot Cu(OH)_2$, used as a pigment.

BLUE, PRUSSIAN. *Chinese blue, Antwerp blue, Berlin blue, Paris blue, soluble blue, bronze blue, Saxon blue.* This pigment occurs in several forms. Commonly it is a mixture of potassium ferric ferrocyanide, $K_2Fe_4(CN)_{12}$, with ferric ferrocyanide, $Fe_7(CN)_{18}$, but the most permanent form is ferric ferrocyanide.

BLUE, SAXON *v.* BLUE, PRUSSIAN.

BLUE, THÉNARD *v.* BLUE, COBALT.

BLUTMEHL *v.* BLOOD.

BLUTWURST *v.* BLOOD.

BOEHMITE or BÖHMITE. An orthorhombic modification of aluminium hydroxide, $Al_2O_3,H_2O{=}AlHO_2$, dimorphous with diaspore (also orthorhombic $AlHO_2$), but differing in its optical properties and in crystal-structure as shown by the patterns in X-ray photographs. It is isomorphous with lepidocrocite in the isodimorphous series diaspore-boehmite and goethite-lepidocrocite. It was first recognised in French bauxite by J. Böhm (Z. anorg. Chem. 1925, **149**, 203) and was named boehmite by J. de Lapparent (Compt. rend. 1927, **184**, 1661). The aluminium hydroxide precipitated from a boiling solution is boehmite, and this on dehydration yields γ-Al_2O_3. L. J. S.

BOG-BUTTER. In various northern European countries, particularly Ireland and Scandinavia, it appears to have been common practice in the Middle Ages to bury butter, or immerse it in peat-water, in order to preserve it or, perhaps, in order to improve (?) the flavour. Specimens of such buried butter, which may date from the eleventh to the eighteenth centuries, are still occasionally discovered in peat-bogs in an advanced state of decomposition, forming the whitish, waxy mass resembling adipocere (*q.v.*), known as bog-butter. Bog-butter has a lower iodine value (*e.g.* 9–15) and higher acetyl value than fresh butter-fat, and consists chiefly of saturated and oxidised (hydroxylated) fatty acids, which have been formed from the original butter-fat as a result of the hydrolysing and oxidising action of water, air, bacteria, and moulds ; as a rule, the bulk of the lower, volatile fatty acids, which characterise fresh butter-fat, have disappeared. Minor amounts of nitrogenous matter (derived from the casein of the butter) and metallic contaminants derived from the water may be present.

It is interesting to note that cholesterol has been recovered from the unsaponifiable matter of bog-butter, having apparently suffered little or

no alteration Analyses of Irish bog butters are recorded by Radcliffe and Maddocks, J S.C.I. 1907, 26, 3, and P. S. Arup, Analyst, 1932, 57, 300; *cf.* S Schmidt Nielsen, Kong. Norske Videnskab Selskab. Forhandl. 1928, 1, No. 61, 182 (Scandinavian and English samples in Norwegian) For the archæology of bog-butter, *see* W. R. Wilde, Proc. Irish Acad. 1856, 6, 356, Gogan, Irish Times, May 16, 1929 (*cf* Arup, *l c.*). E L

BOGHEAD COAL *v.* PARAFFIN

BOGHEAD NAPHTHA *v* PARAFFIN.

BOG-IRON-ORE. An impure iron hydroxide of recent formation in bogs and marshes. It is referable to the mineral species limonite ($2Fe_2O_3,3H_2O$), and, in fact, this name (from λειμών, a meadow) was at first applied to this material, which is known in German as Raseneisenstein or Wiesenerz (meadow-ore) It is sometimes placed under the species limnite (from λίμνη, a marsh), to which the formula $Fe_2O_3,3H_2O$ has been assigned. It contains 20–78% Fe_2O_3, some silica and organic matter, and often phosphates in considerable amount The material has been deposited by the oxidation of chalybeate waters through the agency of algæ and bacteria It is dug in shallow pits in the peat-bogs of Ireland, the production amounting to a few thousand tons per annum, and is mainly used for the purification of coal gas. The Swedish lake ores (*sjomalm*) *are of the same nature* L. J. S.

BOG MANGANESE. *Wad*, a black, earthy mineral consisting mainly of hydrated manganese dioxide, but of variable composition.

BOHEMIAN BOLE. A yellow variety of bole (*q v*)

BOHNALITE *v.* ALLOYS, LIGHT.

BOHN-SCHMIDT REACTION *v.* ALIZARIN AND ALLIED DYESTUFFS

"BOILED KEENE'S" PLASTER *v.* BUILDING MATERIALS, Section II.

BOILED OIL. Boiled linseed oil. Formerly denoted a preparation obtained by heating linseed oil with about 0 5% litharge, PbO, for several hours to 200°–250° with access of air. Other drying agents, *e.g.* manganese borate, can be used instead of litharge. The product, "kettle boiled oil," dries much more rapidly than the raw oil and is used in paints (*cf.* British Standards Specification 242, 1936). The term "boiled oil" also includes linseed oil containing drying agents added in solution, *e g.* linoleates of lead, manganese or cobalt dissolved in a part of the oil. These preparations made with little or no heating, which are sometimes termed "bung hole boiled oils," have the property of rapid drying and are used for this purpose in paints.

BOLDO LEAVES. The dried leaves of an evergreen tree, *Peumus boldus*, of central Chili, contain the alkaloid *boldine* (0·1%), the glycoside *boldin* or *boldoglucin*, a volatile oil (2%) containing terpenes and terpineol. The tincture has diuretic and stimulant properties due to the volatile oil (B P.C. 1934).

BOLE. (*Bol*, Ger.) A ferruginous clay-like substance, of red, brown or yellowish colour. It is not plastic, and when thrown into water falls to pieces with emission of streams of minute air-bubbles. It has an unctuous feel, and some varieties adhere to the tongue. When cut it presents a shining streak. Before the blowpipe it fuses to a yellowish or white enamel. Its composition is very variable, but the usual limits are from 41 to 47% SiO_2, 18 to 25% Al_2O_3, and 24 to 25% H_2O, with a proportion of Fe_2O_3, which may reach 12%. It will be noticed that the percentage of water is higher than in clays. The *Fettbol* of Freiberg in Saxony occurs in mineral veins, and contains only about 3% of Al_2O_3. The bole of Stolpen in Saxony is a yellowish substance containing only a trace of Fe_2O_3. Rammelsberg's analysis yielded SiO_2 45 92, Al_2O_3 22 14, CaO 3 9, H_2O 25 86. In the "bole of Sinope" (sinopite) from Asia Minor the SiO_2 falls as low as 32%. The ancients obtained this material from Cappadocia, and used it as a red pigment. It was also employed in medicine as an astringent (*v.* LEMNIAN EARTH).

Bole is frequently found as a product of the decomposition of basaltic rocks. Thus the sheets of basalt of N.E. Ireland, representing Tertiary lava-flows, are separated by partings of bole, associated with lithomarge, bauxite, pisolitic iron-ore and seams of lignite. The Antrim bole is described as a poor variety of aluminous iron ore (G. A. J. Cole, "The interbasaltic rocks (iron ores and bauxites) of north-east Ireland," Mem. Geol. Survey, Ireland, 1912) L. J. S

BOLOGNAN (*Bononian*) **STONE.** A native variety of barium sulphate found as nodular masses embedded in clay near Bologna; when partially reduced to sulphide by calcination with charcoal it exhibits phosphorescence. Vanino and Zumbusch (J. pr. Chem. 1911, [ii], 84, 305) have attempted to ascertain the factors which determine the phosphorescent quality of Bologna stones. Good samples may vary in sulphur content between 12 and 33%. Marked phosphorescing power seems to depend upon the presence of polysulphides; products containing only monosulphide are deficient in this respect. The presence of calcium oxide appears to increase the phosphorescing power (*v.* BARYTES and LUMINOUS PAINTS).

BOLORETIN. A resin derived from the fossil fir wood found in the Danish peat bogs.

BOMBICESTEROL, $C_{26}H_{43}\cdot OH,H_2O$, m.p. 148°, $[\alpha]_D^{15}$ −34°, a member of the cholesterol group occurring in the unsaponifiable portion of chrysalidine oil extracted from the chrysalis of the silkworm (*Bombyx mori*). (Menozzi and Moreschi, Atti R. Accad. Lincei, 1908 [v], 17, 95.)

BONE. Bony tissue may be either compact as in the shafts of the long bones, or spongy or cancellated as in the flat bones of the skull and in the extremities of the long bones; here an external compact layer encloses a mass of spongy bone or diploë. From the embryological point of view, bones may be divided into cartilage bones and membrane bones. The cartilage bones are those which in embryonic life are preceded by cartilaginous prefigurements; these comprise the majority of the bones in the human body, and include all the long

bones except the clavicle. In the case of *membrane* bones (for instance, the flat bones of the cranium) there is no such preliminary cartilaginous prefigurement. In the cartilage bones the cartilage is not converted into bone; for here, as in the cases where there is no cartilage present, the true bony tissue is laid down by the agency of cells termed osteoblasts in the connective tissue sheath (periosteum) of the bone, and the cartilage when present, after undergoing a certain amount of calcification, is then entirely eaten away by large cells called osteoclasts. In the cartilaginous, as distinguished from the bony or teleostean fishes, the replacement of the cartilage by true bone does not occur.

Bone is deposited in concentric laminæ, the majority of the layers encircling the channels called Haversian canals, in which the blood-vessels lie. The living elements in bone, the bone cells, lie in spaces between the laminæ, and these spaces (lacunæ) intercommunicate by minute canals, in which lymph flows and maintains their nutrition.

The chemical materials present are organic and inorganic. The organic materials are proteins and nucleoprotein derived from the bone cells, a small quantity of an elastin-like substance which forms a lining to the Haversian canals, and a mucin or gluco-protein ; but the principal organic material, sometimes misnamed bone cartilage, is better termed *osseïn.* Osseïn is identical with the *collagen* of connective tissues, and like it yields gelatin on boiling with water. If the inorganic salts are dissolved out by mineral acids, the osseïn remains as an elastic mass which preserves the original shape of the bone.

The inorganic constituents remain as the so-called bone earth after the bone is completely calcined ; it consists chiefly of calcium phosphate, but also contains calcium carbonate, and small amounts of magnesium, chlorine, and fluorine. Gabriel (Z. physiol. Chem. 1894, **18**, 257) states that potassium and sodium also occur. Traces of iron come from the blood in the bone, and of sulphate from chondroitin-sulphuric acid (Mörner, *ibid.* 1897, **23**, 311) of mucin.

Investigators differ as to the manner in which the inorganic substances are combined. Chlorine and fluorine are present in the same form as in apatite ($CaF_2{\cdot}3Ca_3P_2O_8$), and according to Gabriel, the remaining mineral constituents form the combination $CaCO_3{\cdot}3Ca_3P_2O_8$. He gives as the simplest expression for the composition of the ash of bones and teeth the formula $Ca_3(PO_4)_2+Ca_5HP_3O_{13}+H_2O$, in which 2–3% of the lime is replaced by magnesia, potash and soda, and 4–6% of the phosphoric acid by carbon dioxide, chlorine and fluorine.

Zalesky's analyses of the bone earth from different animals show how closely these agree in composition; the results are summarised in the following table, the figures representing parts per 1,000.

—	Man.	Ox.	Tortoise.	Guinea-pig.
Calcium phosphate, $Ca_3(PO_4)_2$	838·9	860·9	859·8	873·8
Magnesium phosphate, $Mg_3(PO_4)_2$. . . .	10·4	10·2	13·6	10·5
Ca combined with CO_2, F, and Cl . . .	76·5	73·6	63·2	70·3
CO_2 (partly lost on calcining)	57·3	62·0	52·7	—
Chlorine	1·8	2·0	—	1·3
Fluorine	2·3	3·0	2·0	—

The various bones of the skeleton differ a good deal in the proportion of water, organic solids, and inorganic solids which they contain. This depends to some extent on the admixture of marrow, blood-vessels, and other formations from which it is difficult to free entirely the osseous tissue proper. The quantity of water in fresh bones thus varies from 14 to 44%, and of fat between 1 and 27%. The quantity of total organic substance varies from 30 to 52%, the remainder being inorganic.

The marrow is from the chemical point of view mainly fat ; its cells yield protein and nucleoprotein.

On a rough average it may be said that two-thirds of the solids consist of inorganic and one-third of organic compounds.

With regard to the minute composition of bones at different ages, we have no very accurate information. Voit found in dogs and Brubacher in children that the water in the skeleton decreases and the ash increases with advance of years. Graffenberger's observations on rabbits confirmed this view.

A great many experiments have been made to determine the influence of food—for instance, rich or poor in calcium salts—on the composition of bone. The importance of a correct balance between the calcium and phosphate intakes has been emphasised. Of outstanding importance are the numerous researches which have culminated in establishing the essential action of vitamin D (calciferol, *q.v.*) in promoting normal ossification and in countering the disease of rickets.

As regards the chemical mechanisms of ossification much remains to be discovered. But the researches of Robison and his colleagues (Biochem. J. 1923, *et seq.*) show that the deposition of calcium phosphate in bone is associated with the presence of a phosphatase. This bone enzyme splits off the phosphoric acid group of organic phosphates, such as glycero- and hexose-phosphoric acids. The great physiological importance of the bone phosphatase has been shown by Fell and Robison (Biochem. J. 1929, **23**, 767), who have demonstrated, in developing chick embryos, a close correlation between the

initiation of ossification processes and the first appearance of the enzyme.

The calcifying mechanism of which this enzyme is the basis is not entirely specific for the calcium salt of bone, although the properties of this salt are very specially appropriate to the function which it fulfils Thus deposits of the phosphates or carbonato phosphates of barium, strontium and magnesium have been produced in the matrix of hypertrophic cartilage by the phosphatase mechanism *in vitro*

Much information has been published regarding variations in chemical composition in *different diseases of bone* Thus in exostoses the inorganic material is usually increased, in rickets and osteomalacia, the proportion of water and ossein to bone earth is raised The somewhat rare occurrence of a curious protein (called Bence Jones protein, after its discoverer) in the urine is almost invariably associated with bone disease (osteomalacia, or malignant new growths) This protein in many of its characters resembles a protease, but is probably derived from the mucin of osseous tissue.

On heating out of contact with air, bone evolves a large quantity of volatile matter (*v.* BONE OIL) which contains ammonia, pyridine bases, pyrrol, nitriles, etc A black residue is left, consisting of the bone ash in association with carbon, which is called animal charcoal (*q v*)

The industrial uses of bone are very numerous and involve a large import trade, not only is the bone itself made into many utensils, but the materials made from the bone (charcoal, bone ash, gelatin, etc) are put to many uses.

Thus animal charcoal or bone black is employed in many chemical operations, in sugar refining, as a polish for silver work, etc.

Bone meal and bone ash are extensively employed as manure and in the preparation of the superphosphates of commerce

The gelatin in an impure form is used in the preparation of paper, silk, furs, etc, and the purer varieties are also put to numerous uses, for instance, as a clarifying agent in the preparation of wines, beers, liqueurs, for food in the preparation of soups, jellies, and puddings, in the making of photographic films, and in bacteriology for the preparation of culture media (*see* Merck's "Waren-Lexikon," arts. Knochen, Knochenasche, Knochenkohle, Knochenöl; H. Ost, "Lehrbuch der Chem. Technologie," 18th ed, 1932, arts. Knochenmehl, Knochenleim; Dammer, "Handbuch d. chem. Technologie," 1898, 5, art. Knochenverarbeitung, 254). J. P.

BONE ASH, BONE EARTH. Calcined bones (mainly calcium phosphate) used in the manufacture of a softer variety of porcelain (English china) (*v.* BONE).

BONE BLACK. The black residue of bone ash and carbon left after heating bones out of contact with air.

BONE FAT is the fatty matter contained in the bones of animals (cattle) and is, commercially, a by-product in the process of working up cattle bones from the meat industry, whether they be required for the manufacture of fancy goods, or bone char, or for the production of glue and gelatin.[1] For all these manufactures the degreasing of the bones precedes all further operations. Fresh bones from the heads, ribs, shoulder blades, etc., of cattle contain from 12–13% of fat, whilst the large thigh bones ("marrow bones") contain as much as 18–20%.

The old process of recovering the fat by boiling out the broken bones with water in open vessels is now only used in small primitive establishments and, according to Zapoleon ("Inedible Animal Fats in the United States," Stanford Univ., 1929), to some extent in American packing houses which deal with absolutely fresh bones. Only about one-half of the fat present in the bones can be recovered by this method, however, and the poor yield, coupled with nuisance due to the bad odours from such a method, led manufacturers in general to abandon "open boiling" in favour of processes in which the bones are treated with open steam in closed vessels under low pressure (2–3 atmos); the time of steaming is made as short as possible so that only small amounts of the nitrogenous glue yielding constituents of the bones shall be extracted by the water, but the yield of fat is some 50% higher than by the "open" method, and only a few per cent. of grease remain in the treated bones. The quality of the fat obtained by either boiling process is about the same, the product varying from a pale, buttery fat of faint odour to a dark, rancid, malodorous grease according to the age and condition of the bones employed. The best qualities of bone fat, including edible grades, are prepared by these methods, especially in the large packing houses of South and North America, where the bones are worked up in the fresh state: in order to obtain the best results, the bones are thoroughly washed before boiling or steaming. Edible bone fat was also produced in Germany during the Great War (*cf.* Eckart, Z. Unters. Nahr. Genussm. 1922, 44, 1). Some manufacturers wash the bones with dilute sulphurous acid in order to check rancidification and to obtain a whiter fat (and a better glue). Rendered bone fats can be bleached, but only the best qualities are likely to yield a good product.

The highest yield of fat is obtained by extracting bones with an organic solvent, whereby the bone tissues remain unimpaired and the whole of the glue-yielding substances can be recovered after the fat has been removed The extraction process is particularly applied to degrease old and low-grade bones, and to remove the residual grease from "packer" bones which have been partially degreased by the boiling or steaming process: the solvents employed are almost exclusively petroleum spirit ("benzine") or Scotch shale oil (b p. 100°–130°C.), although attempts have been made to use chlorinated hydrocarbon solvents

Owing to the porous texture of the bone tissue, which tenaciously retains air within the capillaries, the extraction of the bones is attended with some difficulty, even when, as is preferable, the bones have been dried (to a

[1] The feet (and, in the U S A., the shin bones) of cattle and sheep are rendered separately as the liquid oil obtained from these bones—the *neat's foot oil* of commerce—constitutes a more valuable product than ordinary bone fat.

water content below 10%) before treatment. Various devices to facilitate the penetration of the solvent, such as the introduction of it in the form of vapour, have been proposed (*cf.* von Girsewald, F.P. 430015 ; Savage, B.P. 278891 ; Schlenker, Chem.-Ztg. 1929, **53**, 837 ; Günther, *ibid.* 1930, **54**, 761). The fat obtained by the extraction process is dark-brown and has a penetrating, unpleasant odour : in addition to a considerable amount of free fatty acids, it may contain lime soaps, calcium lactate and butyrate, etc., and less volatile hydrocarbons derived from the "benzine" used as solvent, which are very difficult to remove, even by prolonged steaming. This grade of fat is very difficult to refine, as even when some immediate improvement is obtained, the colour and odour tend to "revert" after a short time. Volland (G.P. 222669) proposes to bleach extracted bone fat by means of barium peroxide : concentrated hydrogen peroxide is claimed to be an effective (although expensive) bleaching agent, and treatment with hypochlorous acid, alkali dichromate or activated bleaching earths has also been advocated (*cf.* E. T. Webb, "Modern Soap and Glycerine Manufacture," 1927 ; Uhl, Seifens.-Ztg. 1929, **56**, 211 ; Eckart, *ibid.* 240).

Whilst the bone fat obtained by the boiling-out or steam-rendering processes can be employed for the manufacture of soap, the fat obtained by solvent extraction is quite unsuitable for this purpose in this country ; on the Continent, however, such benzine-extracted grease is used in small quantities for inferior soaps, especially when the price of alternative fatty materials is high. The bulk of bone fat is, however, used in candle- and stearine-works, where it is hydrolysed by the autoclave or sulphuric acid process, the resultant fatty acids being purified by distillation. Bone fats are also employed in the manufacture of lubricating greases and stuffing greases.

The chemical composition of bone fat lies between that of marrow-fat and of tallow, the iodine value of fresh cattle-bone fat lying between 45 and 60. Eckart (Z. Unters. Nahr. Genussm. 1922, **44**, 1) records the following approximate composition for three samples of pure ox-bone fat : stearic acid 19–21%, palmitic acid 20–21%, oleic acid 53–59%, glycerol 5–10%, unsaponifiable matter 0·5% (*cf.* Fricke, Z. deut. Oel-u. Fett-Ind. 1923, **43**, 401). Linolic acid was not detected by Eckart, but Stadlinger and Tschirch (Chem.-Ztg. 1927, **51**, 667 *et seq.*), who examined a number of purified samples of laboratory-prepared and commercial bone-fats by thiocyanometric analysis, obtained results indicating the apparent presence of from 5 to 10% of linolic acid.

The valuation of bone-fat is carried out in a similar manner to that of tallow, but special precautions are necessary in order to avoid complications due to the presence of large amounts of free fatty acids, calcium salts and calcium soaps which retain water tenaciously (*cf.* Lewkowitsch, "Chem. Tech. and Analysis of Oils, Fats, and Waxes," 6th ed., 1922, **2**, 759, Macmillan & Co.). Total *fatty matter* (including neutral fat, free fatty acids, and fatty acids derived from the lime soaps) may be determined by warming the fat (10 g.) on the water-bath for an hour (with occasional shaking) with a few drops of strong hydrochloric acid (in order to decompose any soaps present) and then extracting the fatty matter with light petroleum (Shukoff and Schestakoff, Chem. Rev., Fett-u. Harz-Ind. 1898, **5**, 5, 21) ; any insoluble impurities can be separated by filtration, and examined. Any *lime* present may be determined by an analysis of the *ash*. The determination of the *unsaponifiable matter* is important ; amounts in excess of about 2% must be regarded as an impurity, indicating the adulteration of the bone fat with wool grease or low-grade waste fats, etc., containing a considerable proportion of unsaponifiable material.

Bone Oil.—Fatty bone oil consists of the more liquid constituents of bone fat, which are separated from the higher melting components ("stearin") by expressing slowly cooled bone fat in filter presses. Bone oil is used as a lubricant and to replace neat's foot oil in the preparation of "fat-liquors" for the leather industries : a high-grade neutral bone oil is an excellent lubricating oil on account of its very low "cold test." (This fatty bone oil must not be confounded with "Dippel's oil," sometimes also termed "bone oil," which is obtained by the destructive distillation of bones in the preparation of bone charcoal.) E. L.

BONE OIL. *Animal oil, Dippel's oil, Oil of hartshorn, Oleum animale empyreumaticum, Oleum cornu cervi, Oleum Dippelii.* (*Knochenöl, Thieröl*, Ger.)

The product obtained by the distillation of bones in the preparation of bone black or animal charcoal. The first mention of an animal oil appears to be in the writings of C. Gesner, 1552, and of A. Libavius (Alchemia Lib. II, Tract II), 1595, whilst J. R. Glauber (1604–1668) also describes the unpleasant-smelling oil derived from the distillation of animal parts. The first consistent steps in the examination of the oil were made by J. Dippel in 1711, and afterwards by O. Unverdorben (1826), who isolated from it four bases which he described as *odorin, animin, olanin*, and *ammolin*. The investigations of Anderson (Trans. Roy. Soc. Edin. 1849, **16**, 123, 463 ; 1853, **20**, 247 ; 1857, **21**, 219) were the first in which the pure pyridine bases present in the oil were obtained.

The bones are first boiled in a large quantity of water, which removes the greater part of the fatty matters ; they are then roughly dried and subjected to dry distillation in iron retorts, similar to those used in the manufacture of coal gas. E. Alexeevski (J. Russ. Phys. Chem. Soc. 1921, **53**, 306) reports that a better yield is obtained using horizontal rather than vertical retorts. Bone black or animal charcoal remains behind, and bone oil distils. The products of distillation are conducted through long iron condensing tubes, and led into receivers, where the crude bone oil collects, together with water. The gases are then passed into a separator containing sulphuric acid to retain the ammonia, and can afterwards be used for heating purposes, or, if passed through purifiers, for illumination.

A typical analysis is as follows (*Alexeevski, l.c.*):

Bone charcoal	68–70%
Bone oil .	5·3–6·8%
Ammoniacal liquor	17–18%
Gases . .	5–8%

The crude oil is separated from the aqueous distillate and is subjected to redistillation. The aqueous liquid consists of a solution of ammonium sulphide, ammonium thiocyanate and cyanide, ammonium carbonate, and small quantities of very volatile organic bases. This is treated with sulphuric acid and afterwards distilled with slaked-lime. The distillate, on treating with solid potash, yields large quantities of ammonia, whilst some oily bases separate out, and are afterwards worked up with the bases contained in the crude oil.

The crude oil is a dark brown, nearly black liquid, having a most offensive fœtid odour, and sp gr 0 970. On subjecting it to redistillation it begins to boil at 80°, when quantities of ammonia come over together with an oil. The temperature rises very gradually to about 250°. From 180° upwards the distillate contains large quantities of ammonium cyanide and ammonium carbonate which tend to choke the condenser. A black resinous tar remains, which is employed in making Brunswick black.

The following substances have been isolated from bone oil by fractional distillation combined with treatment with acids to separate basic from non basic constituents

Chief Constituents	*Subsidiary Constituents.*
Butyronitrile.	Methylamine.
Valeronitrile	Ethylamine
Hexonitrile.	Aniline.
*Iso*hexonitrile.	Pyridine
Deconitrile.	Methylpyridine
Palmitonitrile.	Dimethylpyridine.
Stearonitrile.	Quinoline.
Pyrrole	Phenol.
Methylpyrrole	Propionitrile.
Dimethylpyrrole	Valeramide.
Hydrocarbons C_9H_{14}	Toluene.
Hydrocarbons $C_{10}H_{16}$	Ethylbenzene.
Hydrocarbons $C_{11}H_{18}$	Naphthalene.

(Weidel and Ciamician, Ber. 1880, 13, 65.)

As to the formation of the various compounds in bone oil, the nitriles are formed by the action of ammonia on the fatty acids, pyrrole and the pyrroles are the products of decomposition of the gelatinous substances, and pyridine and its derivatives are condensation products of acrolein, from the dry distillation of the fats, with ammonia, methylamine, etc.

BORACIC ACID or BORIC ACID *v.* Boron.

BORACITE. Borate and chloride of magnesium, $6MgO\ MgCl_2 \cdot 8B_2O_3$, forming small, bright, sharply developed cubic crystals of tetrahedral symmetry, in which the cube faces usually predominate. The crystals are interesting on account of their strong pyro electrical characters, and the optical anomalies which they exhibit. Each cubic crystal is built up of twelve rhombic pyramids, the bases of which coincide with the twelve faces of the rhombic-dodecahedron and the apices meeting in the centre of the group. At a temperature of 265° the birefringence and twin-lamellæ disappear and the crystal is then truly cubic. This affords a good example of an enantiotropic change in state, the cubic modification being stable only above this temperature. The crystals usually occur embedded in gypsum, and are bounded on all sides by bright facets. Sp gr 2 9–3 0, H. 7 (as high as that of quartz). They are found in considerable numbers at Lüneburg, in Hanover, and at Stassfurt, and elsewhere in the Prussian salt-deposits. A massive earthy variety, known as "stassfurtite," occurs as nodules at Stassfurt in quantities sufficiently large for collecting for commercial purposes. L. J. S.

BORAL. Aluminium boro-tartrate.

BORAX. As a mineral, borax,

$$Na_2B_4O_7,10H_2O,$$

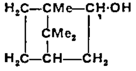
is found as an efflorescence and as monoclinic crystals, sometimes of considerable size, on the shores of the salt lakes of Tibet and California. In San Bernardino and Lake counties in California there are several places known as "Borax Lake"; but most of the borates commercially mined in this region belong to other species (ulexite, colemanite, etc.). The Tibetan deposits extend from the lake-plain of Pugha in the west to the lakes of Tengri Nur in the east, and formerly, since very early times, much crude material was exported under the name of tincal (*v.* Boron). L. J. S.

BORDEAUX MIXTURE. A mixture of lime and copper sulphate used as a fungicide.

"BORIC ACID PHOSPHORS" *v.* Boron, Boric Acid.

"BORNEO-CAMPHOR" *v.* Borneol.

BORNEOL and *iso*BORNEOL.



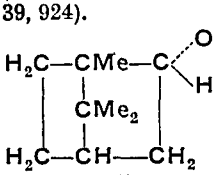
The secondary alcohol, *borneol*, $C_{10}H_{18}O$, owing to its highly crystalline form, was early recognised as a constituent of essential oils and it was frequently confused with camphor. *d*-Borneol, "Borneo-camphor," forms the main constituent of the oil from *Dryobalanops aromatica*, Gaertn, *l*-borneol or "Ngai camphor" occurring in the oil from *Blumea balsamifera*. Both of the optically active modifications and also the racemic form have been found in numerous other oils.

The presence of *iso*borneol has only been recorded in one essential oil, namely, that from *Juniperus excelsa* (Rutovski and Vinogradovo, 1928, B. 768).

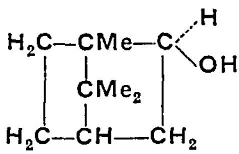
Borneol crystallises in the hexagonal system and it resembles camphor in its odour. The *d*- and *l*- forms have m.p. 208 5°, b p. 212°, $[\alpha]_D$ ±37 92° (in toluene); *dl*-borneol has m p. 210·3°, *d*- and *l*- *iso*borneols melt at 214°, $[\alpha]_D$ ±34 1° (in ethyl acetate). Borneol and *iso*borneol are most conveniently identified by the

preparation of the p-*nitrobenzoates*, melting respectively at 137° and 129° (Henderson and Heilbron, Proc. Chem. Soc. 1913, 29, 281).

The configuration of the alcohols has been the subject of much discussion, but the investigations of Asahina and Ishidate (Ber. 1935, **68** [B], 555 ; 1936, **69** [B], 343) and of Komppa and Beckmann (Annalen, 1936, **522**, 137) show that borneol has the *endo*- configuration (I) and *iso*borneol the *exo*- (II), thus confirming the structures suggested by Vavon and Peignier (Bull. Soc. chim. 1924 [iv], **35**, 925 ; 1926 [iv], **39**, 924).

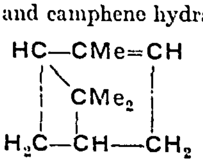


I.

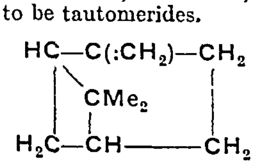


II.

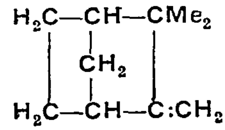
There are available a large number of methods for the preparation of the borneols. Their formation by the reduction of camphor with sodium and alcohol (Jackson and Menke, Amer. Chem. J. 1884, **5**, 270) and by the catalytic hydrogenation of the ketone in the presence of platinum black, when *iso*borneol forms approximately 80% of the product (Vavon and Peignier, Bull. Soc. chim. 1924 [iv], **35**, 925), provides conclusive proof of their constitution. Of fundamental importance was the observation of Bouchardat and Lafont (Compt. rend. 1887, **104**, 1717 ; Bull. Soc. chim. 1887 [ii], **48**, 781 ; Ann. Chim. Phys. 1886 [vi], **9**, 509 ; 1888 [vi], **15**, 145 ; 1889 [vi], **16**, 236) that a mixture of the alcohols was obtained by the hydration of *oil of turpentine* (*α*- *and β-pinenes*). In their original experiments Bouchardat and Lafont showed that when oil of turpentine was heated at 100° with glacial acetic acid a mixture of bornyl and *iso*bornyl acetates was formed, the alcohols being optically active. *iso*Borneol is obtained also, together with some borneol, by the hydration of camphene as was first observed by Kachler and Spitzer (Annalen, 1879, **200**, 340). The hydration of the pinenes and of camphene, so largely utilised in the manufacture of the borneols, an intermediate stage in the manufacture of " synthetic " camphor (*q.v.*) has formed the subject of intensive study and the use of a great variety of reagents has been suggested (*see* Cornubert, " Le Camphre et ses Dérivés," pp. 49 *et seq.* ; Aschan, " Naphthenverbindungen, Terpene, und Campherarten," p. 163). The conversion of α- and β-pinene (III) and (IV) and of camphene (V) into the alcohols involves a Wagner-Meerwein rearrangement and attention is directed to the investigations of Meerwein and his collaborators (*inter alia*, Ber. 1920, **53** [B], 1821 ; 1922, **55** [B], 2506) which have shown the alcohols, borneol, *iso*borneol, and camphene hydrate to be tautomerides.



III.



IV.



V.

The borneols are oxidised very readily to camphor. Technically a catalytic process is employed with a nickel catalyst containing about 10% of cobalt or iron oxide at a temperature of approximately 200°, when the yield of camphor approaches 97%. Oxidation of bornyl acetate with chromic acid gives hydroxyepicamphor (Schrötter, Monatsh. 1881, **2**, 224 ; Bredt and Goeb, J. pr. Chem. 1921 [ii], **101**, 273). By the action of hydrogen chloride in acetic acid on bornyl and *iso*bornyl acetates bornyl and *iso*bornyl chlorides are formed (Kondakov and Schindelmeiser, J. pr. Chem. 1907 [ii], **79**, 569). Dehydration of the alcohols results in the formation of camphene, the loss of water proceeding somewhat more readily in the case of borneol. J. L. S.

BORNEO TALLOW (*Tengkawang-, Sengkawang-fat* : Malay *Minyak Tengkawang*) is a generic term applied to the fats obtained from the kernels of a number of closely allied trees of the genera *Shorea* [1] and *Isoptera* (Fam. *Dipterocarpaceæ*), all of which are indigenous to the Sunda Islands, Malaya and Indo-China. The five species, *S. stenoptera* Burck, *S. lepidota* Bl. (=*S. aptera* Burck), *S. Gysbertiana* Burck, *S. Thiseltoni* King, and *Isoptera borneensis* Scheff, may be mentioned as the most important sources of commercial Borneo tallow, but it has been stated that as many as eighty " varieties " of " tengkawang " are recognised by the natives (*cf.* A. J. Bal, " De Tengkawang in de Westafdeeling van Borneo " ; Landbouw, Buitenzorg, 1933, **9**, No. 5, 211 (summary in Bull. Mat. Grasses, 1934, **18**, 165); Heyne, " De Nuttige Planten van Niederlandsch Indien," 1927, vol. II).

The fruits are collected and shelled by the natives, as only the kernels are exported. In order to facilitate the removal of the hard fruit-shells, these are softened by soaking the fruits for a few weeks in running water (which also effectively kills any insect parasites), or by storing the fruits in heaps in a moist place until germination begins and the shells become ruptured by the young growing shoot ; in some districts the nuts are smoked. The separated kernels are split and dried in the sun and constitute " padi tengkawang " or the so-called (Borneo) Illipé Nuts [2] of commerce, which are exported to Europe (mainly *via* Singapore) for expression. Various commercial varieties of *Shorea* nuts are described in the trade as " Large Black Pontianak Illipé Nuts," " Small Black," and " Large " and " Small " " Brown Pontianak

[1] *Shorea* trees are also sources of resins of the dammar class (*cf.* Wiesner, "Rohstoffe des Pflanzenreiches"; Heyne, "De Nuttige Planten van Niederlandsch Indien," 1927).

[2] These "Illipé Nuts" and "Illipé (=Borneo) tallow" must not be confounded with the true "illipé nuts" of India which furnish the softer "illipé butter," and are derived from the tree *Bassia longifolia* L., N.O. *Sapotaceæ*. See BASSIA FATS.

Illipe Nuts," and "Large" and "Small" "Sarawak Illipe Nuts," the "black" grades being the higher quality and richer in fat. Commercial illipe nuts *also include* "*Small Siak* Illipe Nuts," which are smaller kernels derived from one or more species of the genus *Palaquium* (probably chiefly *Pal. oblongifolium* Burck),[1] which are trees belonging to the same *botanical family, viz. Sapotaceæ*, as the true Indian illipé (*see* BASSIA FATS), *Palaquium* kernel fat should properly be termed Njatua tallow (Malayan "Minyak Nyatoh") or Taban Merah fat.

The tengkawang kernels contain from about 43 to 61% of fat, according to the species and quality. A certain amount of the fat is prepared by the natives for local use as food by boiling out the pounded kernels with water; commercial Borneo tallow is, however, produced in Europe by expression of the kernels, the export of the fat having practically ceased

Borneo tallow expressed from *Shorea* kernels is a hard non-greasy fat, melting at 28°–38°C. and possessing a not unpleasant odour, and a pale green colour which may fade to a pale yellow and ultimately to white on prolonged exposure to light. Apart from its colour, *Shorea* fat closely resembles cacao fat (*q v*) in physical properties. in particular, it displays a similar combination of a low melting point and a characteristic brittle consistency ("snap") which renders it valuable as a substitute for cacao butter in the manufacture of chocolate and confectionery. For the detection of Borneo tallow in cacao fat, *see* Tate and Pooley (*Analyst*, 1921, 46, 229); Knapp, Moss, and Melley (*ibid.* 1927, 52, 452). Whilst the Pontianak and Sarawak nuts are almost exclusively employed for such edible purposes, the white fat from the *Siak varieties is at present mostly consumed* in the manufacture of soap, it would appear from the study of the constitution of this fat by Hilditch and Stainsby (J.S C I 1934, 43, 199) that *Palaquium* fats might also be usable as *substitutes for Borneo tallow in confectionery.* According to Heyne, however, the native-prepared balam fat (from *Pal. walsurifolium* Pierre) has a bitter taste and is unsuitable for edible purposes.

The iodine value of Borneo tallow is about 28–35; the fatty acids have a high melting-point, viz. 52–58°C. In the case of a sample of Borneo tallow, m.p. 36–36 5°C, iodine value 32 3, examined by Hilditch and Priestman (J S.C.I. 1930, 49, 197T), the fatty acids had the following composition: myristic acid 1 5%, palmitic acid 21 6%, stearic acid 38·7%, and oleic acid 38·2%. As in the analogous case of cacao butter (*q.v.*), the peculiar physical characters of Borneo tallow, to which it owes its use as a chocolate fat, are a consequence of its comparatively simple glyceridic composition and the predominance of the mixed glyceride, oleo-palmito-stearin, which, together with oleo-distearin and oleo-dipalmitin, constitutes from 78 to 87% (probably at least 85%) of the fat; about 4 5% of fully saturated glycerides, and only minor amounts, if any, of di oleoglycerides and triolein, are present (Hilditch and Priestman).

Individual fats from *Shorea Gysbertiana* Burck, *Isoptera borneensis* Scheff ("Teglam fat"), and *Sh. Thiseltoni* King, have been described by Brooks (Analyst, 1909, 34, 205), Sprinkmeyer and Diedrichs (Z. Unters. Nahr. Genussm. 1912, 23, 589), and Georgi (Malay. Agric. J 1924, 12, 77).

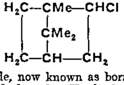
Njatua tallow ("Minyak Nyatoh").—*Palaquium* fat (m p 38°–42°C., iodine value 36–46; *cf* Bull. Imp Inst. 1915, 13, 335; Georgi, Malay. Agric J. 1923, 11, 38; Hilditch and Stainsby, J S C I. 1934, 43, 199) has a higher melting point and contains a higher proportion of stearic acid than the *Shorea* fats, as is shown by the following analysis of the fatty acids of a sample of Njatua fat (probably from *Pal. oblongifolium*) by Hilditch and Stainsby (*l c.*): myristic acid 0 15%, palmitic acid 5 9%, stearic acid 54 0%, oleic acid 39 7%; the fat contained about 77% of mono-oleo disaturated glycerides (mainly oleo distearin) and about 21% of di oleo-stearin. D. L

BORNESITOL, $C_6H_6(OH)_5OMe$, m p. 199°, $[\alpha]_D$ +31 6°, is the monomethyl ether of *l* inositol which is present in Borneo rubber latex It is isomeric with sequoyitol.

E. F. A.

BORNITE. A sulphide of copper and iron, of importance as an ore of copper (Cu 45–71%). On a freshly fractured surface the colour is dark bronze, but this quickly tarnishes to purple or deep reddish; hence the names purple copper-ore, variegated copper-ore (Buntkupfererz), erubescite, and the Cornish miner's name horse flesh ore. Further alteration produces *a black sooty coating.* The *massive ore* is always much intermingled with chalcopyrite, and even the rarely occurring cubic crystals usually contain a nucleus of chalcopyrite The exact composition of the mineral has *therefore long been doubtful*; *analyses by* B J. Harrington (1903) and E. T. Allen (1916) of carefully selected material gave the formula Cu_5FeS_4; this is the bornite of W. Haidinger (1845). Bornite of F. S. Beudant (1832) is an *obsolete synonym of tetradymite or telluric* bismuth L. J. S.

BORNYL CHLORIDE and *iso*BORNYL CHLORIDE.



The chloride, now known as bornyl chloride, was prepared first by Kindt in 1802, who observed that when hydrogen chloride was passed into oil of turpentine a crystalline substance separated to which he gave the name "artificial camphor." It was known subsequently as "pinene hydrochloride" and regarded as a true derivative of pinene although the researches of Berthelot (Annalen, 1859, 110, 37; Compt. rend. 1862, 55, 496) and of Riban (Ann. Chim. Phys. 1875 [v], 6, 23, 363)

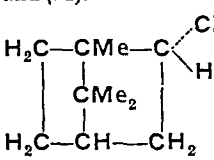
[1] This is now considered to be a race of the gutta-percha tree *Pal. gutta* Burck (*cf.* Heyne, "De Nuttige Planten van Nederlandsch Indien," 1927). The fats from *Pal. Burckii* Lam. and *Pal walsurifolium* Pierre are known by the native names of "soentai" and "balam" fats respectively.

rendered this extremely improbable. The true pinene hydrochloride was prepared by Aschan (Ofvers. Finska Vet.-Soc. 1914, **57**, No. 11) and by Meerwein and Emster (Ber. 1922, **55** [B], 254).

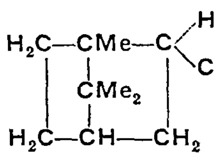
*iso*Bornyl chloride was obtained first by Berthelot (*l.c.*) by the action of hydrogen chloride on camphene.

Bornyl chloride crystallises in leaflets, m.p. 132°, b.p. 207°–208°, $[\alpha]_D$ $\pm$33·5° (in alcohol). *iso*Bornyl chloride melts at 161·5° although lower melting-points have been recorded, since it is very difficult to obtain this chloride quite free from traces of camphene hydrochloride and bornyl chloride. It appears doubtful if it has been obtained optically pure.

Since the two chlorides can be prepared respectively from borneol and *iso*borneol (*q.v.*) by replacement of the hydroxyl groups by chlorine, as was first observed by Wagner and Brickner (Ber. 1899, **32**, 2302), it follows that they must be the *endo-* and *exo-* forms represented by (I) and (II).



I.



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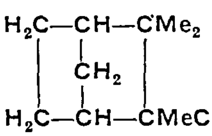


III.

The formation of bornyl chloride from pinene and of *iso*bornyl chloride from camphene involves a Wagner-Meerwein change, and, as Meerwein and Emster (Ber. 1920, **53** [B], 1821; 1922, **55** [B], 2056) have shown, bornyl chloride, *iso*bornyl chloride, and camphene hydrochloride (III) are tautomerides. This explains the difficulties encountered in their purification.

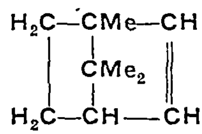
In view of its industrial importance, the best conditions for the preparation of bornyl chloride from pinene have been carefully studied. It is essential for high yields that both the hydrogen chloride and the hydrocarbon should be rigorously dried and also that the temperature during the passage of the gas should not exceed 30°. Vigorous stirring also improves the yield. As a general rule this is approximately 55–65%, although yields up to 75–85% have been obtained in the laboratory (Pariselle, Compt. rend. 1923, **176**, 1901). Bornyl chloride can be obtained also by the action of hydrogen chloride or phosphorus pentachloride on borneol.

*iso*Bornyl chloride is prepared most conveniently by the action of hydrogen chloride on camphene. The primary product of the reaction is here camphene hydrochloride, but this substance isomerises readily. If, therefore, the reaction is carried out in either ethyl or methyl alcohol solution fairly pure *iso*bornyl chloride crystallises out. The chloride can be obtained also by the action of hydrogen chloride or phosphorus pentachloride on *iso*borneol.

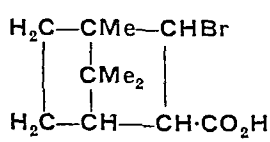
Elimination of hydrogen chloride from either of the chlorides gives camphene, the loss of hydrogen chloride occurring with somewhat greater facility from *iso*bornyl chloride. Whilst this elimination can be effected with all alkalis, technically sodium stearate, phenate or cresolate are as a rule used; the reaction is carried out under pressure at a temperature of about 200°. The yield of camphene is in the neighbourhood of 90%.

The chlorides are highly resistant to oxidising agents. With nitric acid they give ketopinic acid (Armstrong, J.C.S. 1896, **69**, 1397) and camphoric acid (Gardner and Cockburn, *ibid.* 1898, **73**, 278). Reduction of either of the chlorides gives the parent hydrocarbon, camphane. J. L. S.

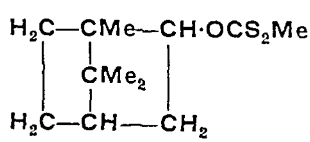
BORNYLENE,



The hydrocarbon, *bornylene*, which does not appear to occur in nature, is known in both optically active modifications; *d*-, m.p. 113°, b.p. 146°, $[\alpha]_D$ −21·69° (in toluene, *c*, 10·45); *l*-, m.p. 109°–109·5°, b.p. 146·5°/756 mm., $[\alpha]_D$ +19·29° (in toluene, *c*, 12·75). It can be readily characterized by the preparation of the *nitrosite*, m.p. 163° (Henderson and Heilbron, J.C.S. 1911, **99**, 1891). Although bornylene was prepared as long ago as 1879 by Spitzer (Annalen, 1879, **197**, 129) by the action of sodium on 2:2-dichlorocamphane, pure *l*-bornylene was first obtained by Bredt and his collaborators (Annalen, 1909, **366**, 1; J. pr. Chem. 1911 [ii], **84**, 778; 1931 [ii], **131**, 137) by the action of heat on the sodium salt of *d*-2-bromocamphane-3-carboxylic acid (I). The yield is, however, poor. The hydrocarbon can be obtained also,



I.

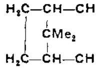


II.

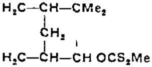
in a somewhat less pure form, by the distillation of methyl bornyl (or *iso*bornyl) xanthate (II) (Tschugaev, J. Russ. Phys. Chem. Soc. 1900, **32**, 332). Bornylene prepared by this method is contaminated with *tricyclene*, which can, however, according to Henderson and Caw (J.C.S. 1912, **103**, 1416), be removed by oxidation with hydrogen peroxide. The hydrocarbon obtained by this method is opposite in sign to the alcohol used for its preparation. Bornylene

is formed also in a number of other reactions (Grignard, Bellot, and Courtot, Ann. Chim. Phys. 1919 [ix], 12, 374; Aschan, Ber 1912, 45, 2396; Ruzicka, Helv Chim. Acta, 1920, 3, 748). On oxidation bornylene yields camphoric acid, thus confirming the structure assigned to it. J. L. S

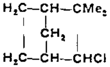
*apo*BORNYLENE.



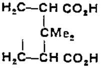
This hydrocarbon, C_9H_{14}, m p 35 5°–36°, b p. 136°–137°/755 mm, is formed when methyl camphenilyl xanthate (I) is distilled (Wagner and Lemischewski, Beilstein, "Handbuch der Organischen Chemie, 4th ed, 5, 123) and also when camphenilyl chloride (II) is warmed with potassium phenate (Lipp and Daniels, Ber *1936, 69, [B], 586). In both these reactions*



I.



II.



III.

a Wagner-Meerwein rearrangement is involved. On oxidation with potassium permanganate the hydrocarbon yields *cis* apocamphoric acid (III). J. L. S

BORNYVAL. Trade name for bornyl *iso*valerate, $CHMe_2{\cdot}CH_2\,CO_2C_{10}H_{17}$, b p 255°–260°. Used in the treatment of neurasthenia.

BORNYVAL, NEW. Neobornyval. Bornyl *iso*valeroylglycollate,

$$C_4H_9CO\,OCH_2\,COOC_{10}H_{17},$$

a substitute for Bornyval (*q v*).

BOROCAINE. *A boric acid salt of* β-diethylaminoethyl *p*-aminobenzoate (procaine, novocaine, ethocaine),

$$(C_{13}H_{20}N_2O_2)_2{\cdot}5B_2O_3,4H_2O.$$

Local anaesthetic. *β-Borocaine*,

$$C_{15}H_{21}NO_2{\cdot}5HBO_2,$$

a boric acid salt of benzamine (betacaine, -eucaine), 4-benzoyloxy-2.2.6-trimethylpiperidine (Extra Pharmacopœia, 1932–1935).

BOROCARBON. Trade name for corundum.

BORO-GLYCERINE. A mixture of glyceryl borate, glycerol, and boric acid containing about 50% boric acid, prepared by heating 320 g. boric acid with 640 g. glycerol to a temperature below 150° until the total weight is 850 g., and after cooling adding 160 g. boric acid. (B P.C 1934)

BORON, so named by H. Davy in 1812, is the element of atomic number 5 at the head of the third group of the periodic table. Its atomic weight is 10 82, resulting from the presence of two isotopes ^{10}B and ^{11}B in boron and all its compounds. Boron is trivalent in the borates and in BCl_3, but not in the borides of the series B_6X (where X is mono-, di-, tri, and tetravalent), and in the hydrides B_2H_6 and B_4H_{10} "The electronic structure of these hydrides is still uncertain, but there seems to be no escape from the view that some of the hydrogen boron attachments are singlets involving only one electron. As each singlet is equivalent to half a co valency it may be said that the theory of integral valencies which was founded by Kekulé on the hydrocarbons has now foundered on the hydroborons." (G. T. Morgan "A Survey of Modern Inorganic Chemistry," Inst. Chem. Lecture, 1935, 56; *cf.* W. Wardlaw, Ann. Report Chem Soc. 1934, 110; Morgan and Burstall, "*Inorganic Chemistry*," p. 87, *Heffer*, Cambridge, 1936.)

Boron does not occur in the free state. Crude borax or tincal, $Na_2B_4O_7,10H_2O$, came to Europe from Asia in the Middle Ages. In 1702 Homberg separated from it a substance which he named *sal sedativum*; this was recognised as the *acid of borax by Baron in 1747. (For the history* of boron, *see* J. W. Mellor, "Inorganic Chemistry," 1924, V, 1.) The element was isolated but not at first studied by H. Davy, who electrolysed moist boric oxide (Phil. Trans 1808, 98, 43; 1809, 99, 75). Gay-Lussac and Thenard (Ann. Chim. Phys. 1808 [i], 68, 169) heated boric oxide with potassium in a copper tube and published the earliest description of the properties of the element. Berzelius determined the proportion of oxygen in boric oxide (Pogg Ann. 1824, 2, 113), and Avogadro (Mem. Accad Sci. Torino, 1821, 26, 1), reasoning from J Davy's value for the vapour density of boron fluoride (Phil. Trans. 1812, 102, 366) deduced its *formula to be* BF_3 and that of boric oxide *as* B_2O_3, and thus enabled many boron compounds to be formulated.

Occurrence.

Boron is widely diffused in nature although its total proportion in the earth's crust (sea included) was estimated by F. W. Clarke and H. S. Washington (Proc. Nat. Acad. Sci. Washington, 1922, 8, 114) as not exceeding 10 p p m. Ocean water contains 15 g. B_2O_3 per cubic metre according to K. Buch (Nature, 1933, 131, 688), a quantity sufficient to influence the carbonic acid equilibrium. V. M. Goldschmidt and C. Peters (Nachr. Ges. Wiss. Göttingen, 1932, 402, 528) found 0 1% B_2O_3 in argillaceous sedimentary rocks, 0 001% in granites, and a smaller percentage, 0 0005% in meteorites. Boron lines have been observed in the spectrum of sun spots (S. Nicholson and N. G. Perrakis,

J. Phys. Radium, 1929, [vi], **10**, 49). It appears to be a constituent of all vegetable and animal organisms (*cf.* ASH, Boron). It is found in fruits, common vegetables, fungus, flour, tobacco, hops, beer, grapes, wine, etc. (Jay, Compt. rend. 1895, **121**, 896; 1914, **158**, 357). Fruits contain 28–112 mg. boric acid, H_3BO_3 per kilo of dry material, wheat flour 2·8 mg. (G. Bertrand and H. Agulhon, Compt. rend. 1914, **158**, 201; G. Bertrand and de Waal, *ibid.* 1936, **202**, 605). They found in 1 kg. of fresh material, horse muscle 0·07 mg., rabbit muscle 0·16 mg., white of egg 0·79 mg., yolk 0·45 mg., beetroot 432 mg. Cow's milk contained 1·1 mg., human milk 0·45 mg. boric acid per litre (Bull. Soc. chim. 1914, [iv], **15**, 292). S. Dodd (Analyst, 1927, **52**, 459) found 0·01% boric acid in chocolate and 0·02 to 0·08% in cocoa beans and cocoa.

A small proportion of boric acid is of critical importance for the growth of plants, even 0·5 mg. per litre of nutrient medium had a marked effect on the development of the tropical lily *Nymphæa*, T. Schmucker (Naturwiss. 1932, **20**, 839). A deficiency in boron is associated with diseased conditions in apples, sugar beet, corn, turnips and tomatoes. Growth is, however, inhibited by excessive amounts of boric acid. With lettuce 0·4 to 0·7 p.p.m. in the culture gave vigorous growth; concentrations of 1·0 to 2·5 p.p.m. were increasingly toxic (J. S. McHargue and R. K. Calfee, Plant Physiol. 1933, **8**, 304; *see also* L. G. Willis, "Bibliography of References to the Literature on the Minor Elements and their Relation to the Science of Plant Nutrition," 1935, 275, with many references to boron).

The use of boric oxide as a food preservative is now illegal in Great Britain (Statutory Rules and Orders, 1925, No. 775; 1926, No. 1557; 1927, No. 577; Public Health (Preservatives, etc., in Food) Regulations, 1925).

Boron Minerals and Sources.—Boric acid or boracic acid, H_3BO_3, occurs as the mineral sassolite, triclinic crystals, found in volcanic craters and abundantly in solution in the Tuscan lagoons, whence it is extracted. Borax (*q.v.*), $Na_2B_4O_7,10H_2O$, is deposited by the salt lakes of California and Tibet. Colemanite, a hydrated calcium borate, $Ca_2B_6O_{11},5H_2O$ (California), ulexite or boronatrocalcite (*q.v.*), $NaCaB_5O_9,8H_2O$ (Chili, Argentine), and pandermite, $Ca_5B_{12}O_{23},9H_2O$ (Turkey) are mined and exported. Borocalcite, $CaH_2B_4O_8,3H_2O$, and laderellite, an ammonium borate, $(NH_4)_2(B_5O_8)_2,5H_2O$, are found in Tuscany. Boracite (*q.v.*) collected and marketed in Stassfurt has the formula $(Mg_3B_8O_{15})_2MgCl_2$. Magnesium borates, considered to be transformation products of boracite, are pinnoite, $MgB_2O_4,3H_2O$, ascharite, $MgHBO_3$, and kaliborate,

$$KMg_2B_{11}O_{19},8H_2O.$$

The gem tourmaline is a complex borosilicate of aluminium (for boron minerals *v.* Doelter, Mineralchemie, 1926, III, ii, 375–435). The fumaroles or soffioni, jets of superheated steam (100° to 190°) escaping from the earth in Tuscany, are an important source of boric acid, the condensed water deposits about 7 g. per litre of boric acid, and retains in solution about 0·5 g. The jets are piped and drive turbo-generators and thus furnish electric power for the district (P. Ginori-Conti, "Utilizzazione dei soffione boracifera di Larderello ad energia industriale," Florence, 1917; G. Ginori-Conti, "L'industria boracifera. I progress idell' industria chimica italiana nel 1° decennio di regime fascista," ed. D. Marotta, Rome, 1933).

PREPARATION.

H. Davy (Phil. Trans. 1809, **99**, 37) obtained boron on the cathode as a dark combustible powder when moist boric oxide was electrolysed between platinum poles. A long series of methods then followed in which powdered fused boric oxide was heated with reducing agents. Gay-Lussac and Thénard (*l.c.*) heated a mixture of boric oxide and potassium in a copper tube. The method was modified by Berzelius (Pogg. Ann. 1824, **2**, 139). F. Wöhler and H. St. Claire Deville employed a mixture of boric oxide and sodium which was covered with sodium chloride and heated in an iron crucible (Compt. rend. 1857, **45**, 888). H. Moissan found that the boron obtained by these methods was very impure, even after repeated extraction with boiling hydrochloric acid. A product prepared by Wöhler and St. Claire Deville's method contained only 71·97% B (Ann. Chim. Phys. 1895, [vii], **6**, 299). W. Kroll (Z. anorg. Chem. 1918, **102**, 10) improved the sodium reduction method by the substitution of a nickel crucible for iron, the employment of a lower temperature and the exclusion of furnace gases. The product purified by extraction with hydrochloric and hydrofluoric acids contained 0·1% nickel and 3·8% sodium but as much as 20% oxygen. With calcium as the reducing agent instead of sodium the product was calcium boride, containing, after acid treatment, 30·5% Ca. The reduction of boric oxide by magnesium, tried without success by C. Winkler (Ber. 1890, **23**, 772), was investigated by Moissan (Ann. Chim. Phys. 1895, [vii], **6**, 307), who, to avoid insoluble borides, employed less than the theoretical proportion of magnesium in the first stage of the process. Three parts of anhydrous boric oxide and one part of magnesium filings heated to bright redness in a clay crucible (preferably lined, *v. infra*) yielded a melt containing a brown core. This portion was pulverised and boiled successively with water, hydrochloric acid, alcoholic potash, water, and hydrofluoric acid (50%). The washed and dried residue contained 93·97–95% B and 2·28–4·05% Mg. For further purification it was then strongly heated with fifty times its weight of boric oxide in a crucible lined with a mixture of carbon and titanic oxide. The mass obtained by this second fusion was purified as before. Moissan claimed for the final product a purity of 99·2–99·6%. The process gives a small yield and is very tedious. This "classical" method for the preparation of amorphous boron has been criticised by Stock and Holle (Ber. 1908, **41**, 2099) who obtained boron of only 86%, similarly Weintraub, 88–90% (Trans. Amer. Electrochem.

Soc 1909, **16**, 167), W. Kroll (Z anorg Chem 1918, **102**, 2) following the directions of Moissan and Weintraub and taking many precautions prepared boron analysing 91 6%. B. L Hackspill (Helv Chim. Acta, 1933, **16**, 1111) defends the method, provided that the original directions are rigorously carried out. A Binet du Jassonneix (Ann Chim Phys 1909, [viii], **17**, 161) shortened the process by levigation with water, the borides being specifically heavier than boron Prolonged treatment of the lighter fraction with hydrochloric, hydrofluoric, and sulphuric acids yielded a brown powder containing 97 1% boron

R C Ray (J C S 1914, **105**, ii, 2162) claims to have prepared crystalline boron (B 98 10%, Si 2 16%), insoluble in warm dilute nitric acid, by heating Moissan s amorphous boron in a current of hydrogen with excess of magnesium or sodium, and subsequently volatilising all the free and combined metal at a higher temperature In agreement with Weintraub (*l c*) and Kroll (*l c*) Ray found that amorphous boron contains considerable quantities of oxygen The appearance of the crystalline boron is not described by the author E. Weintraub working with crude boron obtained by reduction with magnesium which had the approximate composition of a suboxide B_8O (Trans Amer. Electrochem Soc. 1909, **16**, 165) carried out the first technical preparation of the element Several pounds of the boron were fused in a copper cup heated by an electric arc (200–300 amperes at 500 volts D C) in a hydrogen atmosphere. The impurities, magnesium, nitrogen, and oxygen, volatilised and the residual boron was of 97 to 98% purity (Ind. Eng. Chem. 1911, **3**, 299, 1913, **5**, 106)

E. Podszus (Z. anorg Chem 1917, **99**, 25) ground together anhydrous boric oxide with magnesium in slight excess of the theoretical quantity. The mixture was then fired in an atmosphere of coal gas The upper layer of the fused mass was rejected and the remainder purified by extraction with boiling hydrochloric acid and water. The boron obtained was only 70% pure, but is suitable for the preparation of boron trichloride (*v.* p. 43).

Sulphur was added to the mixture by K A, Kuhne (G.P 147871, 1902, and 179439, 1904) and by W. Kroll (*l c*) with the object of forming a layer of readily fusible slag to exclude air. Kroll found that boron thus obtained contained very little oxygen.

Reduction of Boric Oxide with Aluminium —"*Crystalline boron*" F. Wöhler and H. St. Claire Deville (Ann. Chim. 1858, [iii], **52**, 68) obtained three varieties of crystals (*a*, *b*, and *c* below) by heating boric oxide with aluminium to a high temperature. These crystals were for long considered to be allotropic forms of boron and were used for determining its physical properties. They are now recognised as borides. (*a*) Black or adamantine boron, very hard, opaque brilliant crystals, their composition corresponds to AlB_{12} (W. Hampe, Annalen, 1876, **183**, 90); (*b*) yellow crystals, like (*a*) they are harder than corundum, and are obtained when the reaction is carried out in a carbon crucible. W. Hampe's (*l.c.*) analysis gave $Al_3C_2B_{48}$. H. Biltz (Ber. 1910, **43**, 297) found $Al_3C_2B_{44}$; (*c*) "graphitoid," thin hexagonal bronze-coloured plates formed at a lower temperature than (*a*) and (*b*) (*cf.* von Náray-Szabó, 1936, A. 273).

F. Wohler and H. St. Claire Deville (Compt. rend. 1867, **64**, 19) state that graphitoid boron does not burn in air at a red heat but acquires a blue colour like steel. Heated in chlorine, it ignites forming boron chloride and aluminium chloride. It is easily soluble in concentrated nitric acid but only very slowly in hot hydrochloric acid or in hot caustic soda solution. Two specimens contained 54 02 and 54·91% of aluminium, corresponding to AlB_2.

Both preparations (*a*) and (*b*) dissolve slowly in hot nitric acid (W. Hampe, *l c*), while the crystalline boron described by R. C. Ray (*l c*) is insoluble.

That the aluminium borides cannot be decomposed by treatment with acids, even by hydrogen chloride at a red heat, to yield boron free from aluminium was shown by W. Kroll (*l c*) (*cf* Kahlenberg, Trans. Amer. Electrochem. Soc. 1925, **47**, 29). The latter states that the action of aluminium on boric oxide ($2Al : B_2O_3$) yields boron with excess of borides, while if the proportions are $Al : B_2O_3$, boron is the chief product. The separation of boron from the accompanying borides was not attempted. K. A. Kuhne (D.R.P. 179403, 1904) fired a mixture of boric oxide, sulphur, and aluminium with a magnesium wire. The cold mass, extracted with water and hydrochloric acid, left as residue a mixture of amorphous and crystalline boron containing aluminium which cannot be purified by acid treatment (Kahlenberg, *l.c.*).

Reduction of Boron Trichloride by Metals—W Kroll (Z anorg. Chem. 1918, **102**, 19) found that sodium (at 610°) and potassium (at 300°) react with incandescence, the resulting metallic borides cannot be decomposed by further treatment with boron chloride. Magnesium reacting at higher temperature also yields metallic boride. Aluminium reduces boron chloride at 1,200°. After treatment with hydrochloric acid, yellowish hexagonal plates of aluminium boride remain, resembling the crystals formerly described as "crystalline boron."

Reduction of Boron Trichloride with Hydrogen.—Dumas and also Liebig tried the effect of heating a mixture of boron trichloride and hydrogen The method remained of little interest until it was developed by Weintraub of the General Electric Company, U.S.A., who was the first to produce pure boron in quantity (Trans. Amer. Electrochem. Soc. 1909, **16**, 165; Ind. Eng. Chem. 1911, **3**, 299; 1913, **5**, 106)

Purified dried hydrogen was passed over the surface of boron trichloride kept in a freezing mixture, so that a large excess of hydrogen was maintained. The hydrogen charged with the vapour then passed through one or more powerful alternating current arcs between cooled copper electrodes. At the high temperature of the arc the following reaction occurs:

$$2BCl_3+3H_2=2B+6HCl$$

The boron forms rod like excrescences on the cathode and is also deposited in the apparatus as a fine dust. Washing with water removes a

trace of boric oxide; it is then over 99% pure. Conditions of success are a considerable excess of hydrogen and the use of electric arcs of large area. L. Hackspill, A. Stieber and R. Hocart (*Compt. rend.* 1931, **193**, 776) maintained a condensed high frequency spark between tungsten or molybdenum poles in an atmosphere of hydrogen mixed with the vapour of boron trichloride. Small coherent rods of boron slowly formed on both electrodes, 0·5 g. being obtained in three hours at 300 watts. Three specimens containing 98·6, 99·5 and 98·8% B had almost the black colour of arsenic and were capable of a high polish, their hardness was almost equal to that of the diamond. A crystalline structure was not visible even after etching with aqua regia, but was revealed by X-ray analysis.

Preparation of Boron by Dissociation of Boron Bromide or Boron Chloride.—F. Meyer and R. Zappner (Ber. 1921, **54**, [B], 550). Boron bromide was prepared from Moissan's boron, and boiled in a glass reflux apparatus so that the vapour passed through a powerful arc maintained between copper poles. The flask contained copper powder in quantity sufficient to combine with the bromine. The inner surface of the bulb and condenser was soon covered with a deep black sublimate of boron, the yield was 0·8 g. from 100 g. BBr_3 in five hours. The purity averaged 99·35%. In N. V. Philips' Gloeilampenfabrieken B.P. 264953, 9/11/25, a tungsten or other metal wire is coated with a coherent deposit of boron by heating the wire electrically to 1,400° in an atmosphere consisting only of the vapour of boron halide, preferably the bromide.

E. Podszus (Z. anorg. Chem. 1917, **99**, 129; 1933, **211**, 41) heated pure iron wire (0·3 mm.) spirals to 800° in the vapour of boron trichloride; by continued heating porous black boron free from iron was obtained.

Electrolytic Methods.—W. Hampe, using a platinum anode and a carbon cathode in fused borax, obtained boron contaminated with carbon as a deposit on the cathode, the boron being a secondary product due to the reducing action of sodium liberated at this pole.

H. H. Kahlenberg (Trans. Amer. Electrochem. Soc. 1925, **47**, 30) found that the electrolysis of fused boric anhydride and of borax was impracticable owing to the high resistance of the baths. Borax gave a slight brown deposit of boron on the cathode. The product contained sodium which could not be removed by boiling hydrochloric acid. Potassium borate gave similar results. A very small yield of boron, considered to be nearly 100% pure, was obtained by electrolysing a bath of 50 g. potassium chloride, 20 g. potassium carbonate with as much boric anhydride as the fusion would dissolve. Zschille ("Dissertation," München, 1913), by the electrolysis of fused borate, could not prepare a better product than one with 61·1% B. L. Andrieux (Ann. Chim. Phys. 1929, [x], **12**, 423) found 56·8% B in the product of electrolysis of borax, while a bath of alumina, boric anhydride, and cryolite gave boron of 82·2%. Finally a product with 92·2% boron was prepared from a bath of magnesia, boric anhydride and magnesium fluoride. The melt at about 1,100° was contained in a carbon crucible which served as anode, the cathode was iron or carbon. The boron was deposited in round masses on the end of the cathode, 50–60 g. being obtained in two hours with a current of 10 amperes. The author regards the method as more convenient than Moissan's (*cf.* 1936, A, 414).

Atomic Data.

Boron Isotopes, ^{10}B and ^{11}B. Variations in the proportions of the isotopes in boron compounds obtained from different parts of the world were shown in the atomic weight determinations of Briscoe, Robinson and Stephenson (J.C.S. 1926, 77):

Source of boron compound.	Atomic weight. From density of B_2O_3	From ratio $BCl_3 : 3Ag$
California . .	10·847	10·841
Tuscany . .	10·823	10·825
Asia Minor .	10·818†	10·818

† Density standard.

(*Cf.* F. W. Aston, "Mass-Spectra and Isotopes," London, 1933.)

Atomic Disintegration.—No less than twelve nuclear reactions of the boron isotopes ^{10}B and ^{11}B are tabulated in the Annual Report of the *Chemical Society*, 1935, 29. Boron under particle bombardment, in various experiments, has produced γ-rays, electrons, positrons, neutrons, α-particles, protons, four radioactive elements ^{9}B, ^{11}C, ^{12}B, ^{13}N, as well as ^{7}Li, ^{8}Be, ^{9}Be, ^{12}C, ^{13}C. ^{10}B has itself been formed from ^{7}Li, ^{9}Be, and ^{12}C, and ^{11}B from ^{10}B and also from ^{14}N. For the production of radioactive boron ^{9}B by Fowler, Delsasso and Lauritsen, *see* Physical Rev. 1936, [ii], **49**, 561. (Mme.) I. Curie and F. Joliot (Compt. rend. 1934, **198**, 254) observed that the emission of positive electrons continued for 14 minutes after removing the source of the α-particles bombarding the boron. These positrons are emitted from the new short-lived element radio-nitrogen derived from the boron nucleus. For the artificial radio-active element ^{12}B, *see* 1936, A. 1174.

Chemical Properties.

Experiments with the amorphous boron made by Moissan's method (*l.c.*) form the chief source of our information as to the chemical properties of the element. The boron preparations of E. Weintraub, Podszus, Hackspill, Stieber and Hocart, which contain about 99% B, have not been studied to nearly the same extent. L. Hackspill (Helv. Chim. Acta, 1933, **16**, 1112) was unable to purchase a specimen of pure boron in commerce, possibly because the costly electric arc methods give only a very small yield. The chemical and physical properties of pure boron are known only imperfectly at the present time. Moissan describes it as a chestnut brown powder, staining the fingers, and capable of being agglomerated under a strong pressure. Heated in hydrogen to about 1,500°, it sinters

slightly and increases in density (Compt rend 1892, 114, 617)

Heated in air boron takes fire at 700°, in oxygen it burns with intense brilliancy; in both cases a layer of boric oxide forms, preventing the entire combustion of the specimen With sulphur it combines with incandescence at 610° forming a boron sulphide decomposable by water Selenium behaves similarly at a higher temperature *Tellurium fused in contact with boron does* not react In dry chlorine at 410° boron burns with vivid incandescence, boron chloride distils together with traces of the volatile chlorides of the metallic impurities, while a small quantity of carbon or of carbon boride is left in the boat In bromine at about 700° there is a similar vigorous reaction Bromine water attacks boron slowly at ordinary temperatures, but it dissolves more rapidly in bromine dissolved in potassium bromide solution Iodine vapour does not act on boron at temperatures up to 1,250°

Formation of boron nitride occurs only at high temperatures, at 900° in a current of pure dry nitrogen, only traces of nitride were formed, but the reaction was rapid at 1,230° Heated with phosphorus, arsenic or antimony boron did not yield compounds Carbon combined with boron only at the temperature of the electric arc Silicon *strongly heated* with boron did not react. The metals of the alkalis can be distilled over amorphous boron without any reaction taking place Magnesium forms a boride at a red heat, similarly silver and platinum, while iron and aluminium react only at a high temperature

Mineral acids have a vigorous action. At 250° sulphuric acid is reduced to sulphurous acid. Nitric acid reacts with incandescence Phosphoric anhydride is reduced to phosphorus at 800° Arsenic and arsenious acids yield arsenic at a red heat. In contact with boron a *warm solution of iodic acid liberates* iodine; a mixture of boron and crystals of iodic acid becomes incandescent when gently heated, and evolves dense vapours of iodine Chloric acid solution is also reduced The halogen acids react with more difficulty. At a dull red heat gaseous hydrogen fluoride forms boron fluoride and hydrogen. Aqueous hydrochloric acid saturated at 0° has no action on boron, but gaseous hydrogen chloride reacts at a bright red heat. Hydriodic acid is without effect up to about 1,250°. Sulphur is liberated from sulphur dioxide at temperatures below redness. Below red heat steam has no action on boron, but the reaction, once started, proceeds violently, the products being boric acid and hydrogen. Carbon monoxide yields carbon and boric oxide at about 1,200°, boron takes fire when heated to dull redness in a current of nitrogen monoxide, under the same conditions *nitrogen dioxide* had no effect.

Boron is a powerful reducing agent for metallic oxides. A mixture of lead peroxide and boron ground in a mortar detonates violently. Sufficient heat is liberated in the reaction between cupric oxide and boron to melt glass. Mixtures of boron with the oxides of tin, lead, antimony or bismuth become incandescent when gently heated, the oxides being immediately reduced. Ferric oxide and cobalt monoxide require a bright red heat for reduction. The alkaline earth oxides are not attacked. Potassium hydroxide fused in contact with boron evolves hydrogen in a violent reaction. Small portions of boron burn with a dazzling light when dropped on to melted potassium chlorate, and this reaction serves as a lecture experiment for demonstrating the affinity of boron for oxygen *Boron reduces* solutions of potassium permanganate, ferric chloride, silver nitrate (forming beautiful crystals of silver), palladium chloride, platinum chloride and gold chloride. Potassium and sodium sulphates are reduced by boron at a dull red heat, becoming incandescent and yielding sulphides. Sodium carbonate is reduced at dull redness and potassium carbonate at a higher temperature, the carbonates of calcium and of barium are not decomposed.

Boron (98–99%), prepared from its trichloride and hydrogen by Weintraub (*l c.*) and by Hackspill, Stieber and Hocart (*l c.*), is black in mass and in powder. *Hackspill states that the* small rods of boron which grow on the electrodes are capable of a high polish, their metallic lustre then recalling that of chromium. Hackspill observed that Moissan's boron changes from brown to black when it is heated in absence of air and that the change is *permanent.* The boron (99 35%) obtained by dissociation of boron bromide by F. Meyer and R. Zappner (*v. supra*) is a very fine deep black powder; exposed to air it gradually approaches the colour of Moissan's boron, while the boron content falls several per cent. Permanent preparations should therefore be sealed in hydrogen or preferably in vacuo after a slow, thorough heating With nitric acid boron of this degree of purity reacts violently with incandescence. E Podszus (Z. anorg. Chem. 1917, 99, 130) mentions the following properties of the black boron obtained by the interaction of iron and boron trichloride. In hydrogen at a red heat, it volatilises completely. Heated very gradually in air with a blow-pipe flame, it burns, leaving a residue of pure white boron nitride. When heated rapidly it burns with a brilliant green flame to B_2O_3, *leaving no residue.* The boron filaments did not melt at the highest white heat obtainable by electric heating.

Fused Boron, prepared by H. H. Kahlenberg (*l.c.*, 54) by fusing compressed Moissan's boron in the oxyhydrogen flame, at a temperature he estimated to be 2,250°, is not appreciably attacked by boiling caustic potash solution or by hot concentrated hydrochloric or sulphuric acids Nitric acid and aqua regia are also practically without action. Fused boron is oxidised by alkaline permanganate, it is rapidly attacked by fused caustic alkalis and sodium peroxide. *Boron* replaces gold, platinum, palladium, *silver*, mercury, copper and lead from their solutions, the last named very slowly. In the electrochemical series boron comes just above lead.

Colloidal Boron.—The dispersion of boron to form a solution which passed through filter paper was observed by H. Davy, Gay-Lussac, Berzelius and others to occur when amorphous boron was washed with water, following treatment with dilute acids and alkalis. Unstable reddish

brown, or stable brown to brownish yellow, boron solutions have been studied. A convenient preparation is described by A. L. Elder and N. D. Green (J. Physical Chem. 1932, **36**, 3085). 0·5–1·0 g. dried boron, prepared by fusing magnesium with boric oxide and purifying the product with hydrochloric acid, is refluxed with 100–250 c.c. water. The resulting solution is extremely resistant to coagulation even by multivalent ions; the boron particles are negatively charged. For earlier preparations see T. Svedberg, "Herstellung kolloidaler Lösungen anorganischer Stoffe," Dresden, 1909, 384.

Physical Properties.

Density.—L. Hackspill, A. Stieber and R. Hocart found 2·33±0·01 at 20° (Helv. Chim. Acta, 1933, **16**, 1114; in Compt. rend. 1931, **193**, 777, a misprint, 3·33), which they say compares with E. Weintraub's value 2·34 at the same temperature (J. Amer. Chem. Soc. 1915, **37**, 1646). Amorphous boron has the density 2·45, according to H. Moissan (Ann. Chim. 1895, [vii], **6**, 311). W. Kroll (*l.c.*) gives a divergent value, 1·731 at 18°.

Hardness.—Fused boron is next to diamond in hardness (Weintraub, Hackspill).

Melting-point.—2,300°, according to Weintraub (Ind. Eng. Chem. 1913, **5**, 114); 2,200° was found by E. Tiede and Birnbräuer to be mean temperature of fusion of amorphous boron in vacuo (Z. anorg. Chem. 1914, **87**, 143).

Volatility.—Boron evaporates perceptibly at 1,200°; at 1,600° the blackening of the walls of the vacuum bulb was such as to render boron filaments useless for incandescent lighting (E. Weintraub, Trans. Amer. Electrochem. Soc. 1909, **16**, 179).

Electrical Conductivity.—E. Weintraub observed a remarkable variation of resistance of fused boron with temperature; in one experiment, from 775,000 ohms at 27° to 4 ohms at 600°, and only a fraction of an ohm above 1,000°, *i.e.* an increase of conductivity of about 10^6 or 10^7 to 1 (*cf.* carbon 2 : 1 and silicon 100 : 1, Trans. Amer. Electrochem. Soc. 1909, **16**, 181; Ind. Eng. Chem. 1913, **5**, 107). A. H. Warth (Trans. Amer. Electrochem. Soc. 1925, **47**, 62) gives similar figures for boron deposited from boron trichloride on a glowing tungsten wire. E. Podszus (Z. anorg. Chem. 1917, **99**, 130; 1933, **211**, 41) on the contrary found only a small negative temperature coefficient. H. H. Kahlenberg (Trans. Amer. Electrochem. Soc. 1925, **47**, 36) found that boron prepared by heating Moissan's boron with aluminium showed a great increase in the conductivity on heating to about 50°. Finally R. Freymann and A. Stieber (Compt. rend. 1934, **199**, 1109) confirmed Weintraub's result, within the temperature range studied, viz. 5°–110°.

Thermal Expansion.—E. Dupuy and L. Hackspill (Compt. rend. 1933, **197**, 229) found the mean coefficient of expansion of boron (99·5% B) to be $8{\cdot}3\times10^{-6}$ between 20° and 750°. There was no anomalous variation with temperature, the curve being almost a straight line.

Specific and Atomic Heat.—Early measurements by Regnault showed that boron did not obey Dulong and Petit's rule. The latest determinations are as follows: −253° to −196°, sp. heat 0·0212, at. heat 0·23 (J. Dewar, Proc. Roy. Soc. 1914, [A], **89**, 168); −190·8° to −78·3°, sp. heat 0·0707, at. heat 0·76; −76·4° to 0°, sp. heat, 0·1677, at. heat 1·81 (E. Koref, Ann. Physik, 1911, [iv], **36**, 64). Dewar does not describe his material. Koref worked with Kahlbaum's "pure amorphous boron." Moissan and Gautier (Ann. Chim. Phys. 1896, [vii], **7**, 568) also using amorphous boron, found at 0°–100°, sp. heat 0·3066, at. heat 3·31, 192·3°, sp. heat 0·3407, at. heat 3·69; 234·3°, sp. heat 0·3573, at. heat 3·87. A. Magnus and H. Danz (Ann. Physik, 1926, [iv], **81**, 407) working with Merck's amorphous boron of 97% purity, found the following expression for the atomi heat between 0° and 900°:

$$C_p=2{\cdot}3658+7{\cdot}9080\times10^{-3}t-4{\cdot}9023\times10^{-6}t^2$$

Spectroscopy.—The persistent lines of boron in the arc spectrum are 2,496·778 and 2,497·733 (International Critical Tables, V, 323), the "raie ultime" is 2,497. The double line enables the detection of traces of boron in plant ashes and rocks (A. de Gramont, Compt. rend. 1918, **166**, 477).

Production.

The following table is taken from "Statistical Summary of the Mineral Industry, 1932–34," Imperial Institute, 1935, 59:

Production of Crude Borates (Long Tons).

	1932.	1933.	1934.
Germany—boracite	—	66	7
Italy—boric acid	5,383	5,356	5,488
United States—borates	162,424	167,899	216,429
Argentine—borate of calcium	879	619	—
Turkey—borates	4,915	7,434	6,409

In 1934 the imports (less re-exports) into the United Kingdom were: borates 14,468, borax 10,849, boric acid 2,083 tons (*ibid.* 62).

United States.—Different sources of boron minerals have been worked and later abandoned. In 1856 borax was obtained from hot springs in

The raw materials for the preparation of boron hydrides are magnesium boride and hydrochloric acid and a number of chemists, *e.g.* F. Jones, Sabatier and Ramsay, examined the mixture of gases evolved without isolating a pure boron hydride, or deducing a correct formula. It was known that the crude gaseous mixture burnt with a brilliant green flame and deposited a brown layer of amorphous boron on a crucible lid, that it reduced silver nitrate and potassium permanganate solutions. Later work showed that the gas was a mixture of hydrogen with small volumes of hydrides of boron and of silicon. A. Stock and his co-workers in a series of papers from 1912 onwards have published almost all that is known of the chemistry and physics of the boron hydrides. A monograph by this author is "Hydrides of Boron and Silicon," Cornell University Press, 1933, vol. 12 of the George Fisher Baker Lectureship, from which the following particulars are quoted; references are to A. Stock's papers unless otherwise stated.

Preparation of Magnesium Boride.—A mixture of magnesium, 8 parts, and boric oxide, 3 parts (both as free as possible from silicon), is heated in an iron crucible through the lid of which a current of pure dry hydrogen is passed; directly the contents begin to glow the crucible is cooled in water. The cold product is finely powdered and fed into 10% hydrochloric acid, or preferably into 8*N*—phosphoric acid (E. Wiberg and K. Schuster, Ber. 1934, **67**, [B], 1805, who found that the yield of boron hydrides was thereby increased from 4·6 to 11·4%). The gases formed by the reaction are washed with water, dried, and then enter two large U-tubes cooled with liquid air, the uncondensed gas, hydrogen and traces of silicon hydride escape through a mercury seal into the air. The condensate contains B_4H_{10}, with small amounts of B_5H_9, B_6H_{10}, traces of $B_{10}H_{14}$, CO_2, H_2S, silanes, and PH_3. The boron hydrides mentioned are isolated by fractional distillation in vacuo in an apparatus from which moisture and lubricating grease are entirely excluded. The hydrides B_2H_6, B_5H_9, and one hydride whose formula is still doubtful, B_6H_{12} ?, are prepared by heating B_4H_{10}. The only solid volatile hydride $B_{10}H_{14}$ is made by heating B_2H_6.

Diborane, B_2H_6, is prepared by heating dihydrotetraborane, B_4H_{10}, to 90°–95° for five hours, condensing the products in liquid air, and fractionating the B_2H_6 at −112°.

H. I. Schlesinger and A. B. Burg (J. Amer. Chem. Soc. 1931, **53**, 4321) separated B_2H_6 from the mixture obtained when a high tension discharge is maintained in a mixture of boron trichloride (or preferably tribromide) and hydrogen at reduced pressure. The boron trichloride is largely converted into B_2H_5Cl, other products being boron, solid hydrides of boron, and a small amount of B_2H_6. On standing B_2H_5Cl dissociates into B_2H_6 and BCl_3 (Ber. 1914, **47**, 3145). The method is shorter than by way of magnesium boride and B_4H_{10} (Ber. 1923, **56**, [B], 789; 1924, **57**, [B], 562). B_2H_6 is a colourless gas of characteristic disagreeable odour, with m.p. −165·5° and b.p. −92·5°/760 mm. (Ber. 1923, **56**, [B], 798). It dissociates very slowly at ordinary temperatures, more rapidly at 100°–200°, into hydrogen and B_4H_{10}. With oxygen it forms an explosive mixture, the reaction is

$$B_2H_6+3O_2=B_2O_3+3H_2O.$$

The gas reacts rapidly with water,

$$B_2H_6+6H_2O=2H_3BO_3+6H_2$$

With potassium hydroxide or its solutions, the the reaction is $B_2H_6+2KOH=2KH_3BO+H_2$. Ammonia gas in excess reacts to form the non-volatile compound $B_2H_6{\cdot}2NH_3$ (Ber. 1926, **59**, [B], 2210), this is soluble in water giving a solution which precipitates Ni_2B from solutions of nickel salts. A. Stock concludes that B_2H_6 is a dibasic acid in the compound $B_2H_6{\cdot}2NH_3$. Chlorine acts explosively on B_2H_6 forming BCl_3. With hydrogen halides, reaction occurs on raising the temperature,

$$B_2H_6+HX=B_2H_5X+H_2$$

These halogen compounds are unstable (Ber. 1913, **46**, 3354; 1923, **56**, [B], 800; Schlesinger and Burg, *l.c.*). B_2H_6 reduces permanganate and salts of silver, copper and nickel; with potassium amalgam it yields the salt $K_2B_2H_6$ (Z. anorg. Chem. 1935, **225**, 225).

Dihydrotetraborane, B_4H_{10}, forms the largest proportion of the hydrides liberated by the action of acids on magnesium boride or on beryllium boride; in the latter case the gas is free from silicon hydrides (Z. anorg. Chem. 1930, **188**, 35). The isolation and purification of B_4H_{10} is rendered difficult by its dissociation at ordinary temperatures, and is carried out by fractionation in vacuo, the fractions being stored in liquid air (Ber. 1923, **56**, [B], 793; 1924, **57**, [B], 565; *see* B. D. Steele and J. C. Mills, J.C.S. 1930, 74, for a preparation from cerium and aluminium borides). B_4H_{10} is a colourless liquid or gas with a peculiar repellant odour. Its m.p. is −120°, b.p. 18°/760 mm. (Ber. 1923, **56**, [B], 789). If pure it does not ignite spontaneously in air. It decomposes slowly at room temperature, the chief products are hydrogen and B_2H_6 (Ber. 1913, **46**, 1962). Sunlight has little influence, but ultra-violet light accelerates the reaction (*ibid. idem.* 3354). At higher temperatures there is a complicated thermal decomposition, varying according to the experimental conditions. B_2H_6 and other boron hydrides were discovered by Stock among the products of the reaction.

It reacts slowly with cold water:

$$B_4H_{10}+12H_2O=4H_3BO_3+11H_2$$

Dilute hydrochloric acid yields the same products; nitric acid reacts with explosive violence. Potassium hydroxide forms hypoborate:

$$B_4H_{10}+4KOH=4KH_3BO+H_2$$

(Ber. 1914, **47**, 810). Excess of ammonia at −70° yields the compound $B_4H_{10}{\cdot}4NH_3$, which heated to 200° yields $B_3N_3H_6$. Sodium amalgam reacts with B_4H_{10} forming $B_4H_{10}{\cdot}2Na$. With alcohol, an exothermic reaction takes place, about 8 volumes of hydrogen for 1 volume B_4H_{10} are evolved and on adding water a further evolution occurs, until a total of 11 volumes of hydrogen, corresponding to complete hydrolysis, is measured.

Since B_4H_{10} readily yields nascent hydrogen it is a powerful reducing agent.

Dihydropentaborane, B_5H_{11}, was isolated in very small quantity from the products of spontaneous dissociation of B_2H_6 which had been kept at room temperature for about six months (Ber 1924, 57, [B], 574, 1926, 59 [B], 2210, *cf* H I Schlesinger and A B Burg, J Amer Chem Soc 1933, 55, 4009). It is a colourless, very mobile liquid which melts at about −129° It decomposes when kept at ordinary temperature depositing $B_{10}H_{14}$, probably $2B_5H_{11}=B_{10}H_{14}+4H_2$ When treated with ammonia it forms $B_5H_9 \cdot 4NH_3$ with loss of hydrogen (*l c*, 59, 2211)

Hexaborane, B_6H_{10}, is separated by fractional distillation from the crude condensate of mixed boron hydrides and silicon hydrides (*v supra*). Two kilos of magnesium boride yielded about 1 g of hexaborane It is a colourless liquid, m p −65 1°, which decomposes slowly at ordinary temperatures liberating hydrogen and depositing yellow crystals of a hydride, apparently $B_{26}H_{36}$ Water slowly hydrolyses B_6H_{10}, but the decomposition is not complete at 90° after 16 hours It dissolves in sodium hydroxide solution (30%) with slight evolution of hydrogen, on acidification the volume of hydrogen liberated corresponds to complete hydrolysis

Pentaborane.—A Stock and E. Kuss prepared B_5H_9 (170 c c) by passing gaseous B_4H_{10} (1000 c c) through a tube heated to 200°, and fractionating the products in vacuo (Ber 1923, 56, [B], 805) (H. J. Schlesinger and A. B. Burg, J Amer Chem Soc 1931, 53, 4331) isolated pentaborane in 20% yield from the products of heating B_2H_6 with hydrogen chloride for 48 hours at 120°–130°. B_5H_9 is a colourless mobile liquid, m p. −46 6°, d^0 0 61, to its disgusting odour is mainly due the repellant smell of crude boron hydride. At ordinary temperatures it dissociates very slowly into hydrogen and a solid hydride, at 300° the chief products are boron and hydrogen. It is very gradually attacked by cold water, and the decomposition is not complete after heating to 90° for 3 days, the reaction being $B_5H_9+15H_2O=5H_3BO_3+12H_2$. The intermediate products (not isolated) are strongly reducing suboxides of boron (Ber. 1923, 56, [B], 802). Pentaborane combines with ammonia forming the solid $B_5H_9 \cdot 4NH_3$, stable at ordinary temperatures.

Dihydrohexaborane, B_6H_{12} (Ber. 1924, 57, [B], 566), an unstable volatile hydride, is considered by A. Stock to exist in very small amount in the decomposition products of B_4H_{10}.

Dekaborane, $B_{10}H_{14}$, is prepared either from B_2H_6 by heating to 115°–120° for 48 hours, or from B_4H_{10} kept at 90°–95° for 5 hours (Ber. 1929, 62, [B], 92); in each case 100 c c yield about 0 05 g. $B_{10}H_{14}$. This hydride forms colourless, slowly volatile, rhombic crystals, m p. 99 7°, b p. about 213°, d^{20} 0 94, insoluble in water, soluble in alcohol, ether, benzene, and carbon disulphide It does not dissociate at ordinary temperatures nor oxidise when exposed to air. When kept for 2 days at 200° followed by 1 day at 250°, it yields an amorphous yellow substance of gross composition BH_{0-6}, which dissolves in water with evolution of hydrogen Dekaborane is very slowly hydrolysed by water at ordinary temperatures, but completely in 36 hours at 100°, the products being boric oxide and hydrogen. Halogens form mixtures of substitution products. Ammonia forms an unstable compound, at −75° no definite compound was isolated, at 120° there was substitution of NH_2 for hydrogen. Dekaborane dissolves in sodium hydroxide solution with evolution of hydrogen, the solution contains a boron suboxide with strongly reducing properties Prolonged heating at 100° converts this oxide into boric oxide; $B_{10}H_{14}$ is scarcely affected by concentrated nitric acid but reduces permanganate.

Besides the boron hydrides described, A. Stock and his school have obtained in very small quantities a number of liquid and solid hydrides; of the latter this author remarks ("Hydrides of Boron and Silicon," 1933, p. 89) "there seems to be a continuous series of such non volatile yellow hydrides that increase in degree of condensation and decrease in hydrogen content. The series finally ends in the brown, boron like substances that are formed at elevated temperatures, *e g*. when B_2H_6 is heated to 300°" (*cf.* Ber 1936, 69, [B], 1456)

TABLE OF THE PROPERTIES OF BORON HYDRIDES AND OF BORON HYDRONITRIDE.

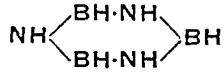
	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	B_6H_{10}	$B_{10}H_{14}$	$B_3N_3H_6$
Boiling-point, °C./760 mm.	−92 5	+18	—	—	—	c. 213	53
Vapour tensions at 0°, mm.	—	388	66	57	7·2	—	84 8
Melting point, °C.	−165 5	−120	−46 6	−129	−65·1	+99 6	−58
Density, *d*. at	0·447	0 59	0 61	—	c. 0 69	0 92	0 824
temperature, °C. . . .	−112	−70	0	—	0	99	0
Parent substance . . .	B_4H_{10}	crude gas. B_2H_5I + Na†	crude gas. B_4H_{10}	B_2H_6	crude gas.	B_4H_{10} B_2H_6	—
Stability	high	low	high	very low	low	very high	extremely high
Decomposition by water .	very rapid	rather slow	slow	—	slow	very slow	rapid

† Ber. 1926, 59, [B], 2226.

Crude gas is the mixture of hydrogen and boron hydrides and silicon hydrides obtained by acting on magnesium boride with hydrochloric acid (A. Stock, Bull. Soc. chim. 1932, [iv], 51, 708; "Hydrides of Boron and Silicon," 1933).

Boron Nitride, BN, is formed when boron is heated in nitrogen, or in air, but is then mixed with boric oxide. It is obtained when boric oxide is strongly heated in contact with carbon and nitrogen (A. Stähler and J. J. Elbert, Ber. 1913, **46**, 2060) or with substances which can supply these elements, *e.g.* cyanogen compounds, calcium cyanide (W. Kroll, Z. anorg. Chem. 1918, **102**, 17), urea (Annalen, 1869, **151**, 255), carbon and ammonia (G.P. 282701). It may be prepared by heating to a high temperature a porous mass of boric oxide and calcium phosphate in the vapour of ammonium chloride, grinding the product and extracting it with hydrochloric acid and with water (L. Moeser and W. Eidmann, Ber. 1902, **35**, 535). Its manufacture affords a means of converting atmospheric nitrogen into ammonia; boric oxide mixed with carbon is heated in a current of nitrogen and the resulting boron nitride converted into boric acid and ammonia by heating with steam to 200°, or by boiling with a solution of sodium hydroxide. E. Podszus describes a continuous process (Z. anorg. Chem. 1933, **211**, 41) in which powdered boric oxide is conveyed down an inclined tube heated to over 1,000°, through which a current of ammonia is passed. Boron nitride is a light, amorphous white powder, a good insulator for heat and electricity. It is said to melt at about 3,000°, but under atmospheric pressure it sublimes before this temperature is reached (Friederich and Sittig, Z. anorg. Chem. 1925, **143**, 293). Phosphorescent boron nitride is prepared by heating the substance with a trace of organic matter, *e.g.* sugar. Boron nitride prepared at a high temperature (1,600°) is much more resistant to water and caustic alkali solution than specimens made at a lower temperature. If it is prepared from borimide at 125°–130°, it is easily decomposed by hot water or by dilute sodium hydroxide or ammonia solutions. Hydrochloric acid in a sealed tube effects complete decomposition (A. Stock *et al.*, Ber. 1901, **34**, 3046; 1908, **41**, 2095). Boron nitride is analysed according to B. Ormont and A. Samoclow (Z. anal. Chem. 1935, **102**, 20) by heating 0·05–0·1 g. to 250° with five times its weight of potasium hydroxide in a porcelain crucible contained in a test tube, through which a current of pure hydrogen is passed. The ammonia liberated is collected in excess of standard acid and titrated.

Boron Hydronitride, $B_3N_3H_6$, is a colourless liquid, m.p. −58°, b.p. 53°. It is prepared by heating the ammonia addition products, $B_2H_6{\cdot}2NH_3$, $B_4H_{10}{\cdot}4NH_3$, or $B_5H_9{\cdot}4NH_3$, to 200° for several hours (A. Stock *et al.*, Ber. 1930, **63**, [B], 2932). It dissociates slowly at 500°C.; heated with water it is hydrolysed to boric acid, ammonia and hydrogen. According to A. Stock its constitution is represented by the formula



Boramide, $B(NH_2)_3$, is formed, mixed with ammonium halide, by the action of boron tribromide on excess of liquid ammonia (A. Stock and W. Holle, Ber. 1908, **41**, 2097), or from boron trichloride vapour carried by a current of hydrogen into liquid ammonia (A. Joannis, Compt. rend. 1902, **135**, 1106). At temperatures above 0° boramide dissociates into borimide and ammonia. The properties of boramide have not been described.

Borimide, $B_2(NH)_3$, can be prepared by dissolving out the ammonium chloride from the decomposition products of crude boramide (A. Joannis, *l.c.*) or by heating the compound $B_2S_3,6NH_3$ to 120° in a current of hydrogen, but preferably by heating boron sulphide-hydrosulphide, $B_2S_3{\cdot}H_2S$, to 75° in gaseous ammonia (A. Stock and M. Blix, Ber. 1901, **34**, 3039). The products from the last two preparations retain a trace of sulphur in spite of boiling with carbon bisulphide. Borimide is a white powder, insoluble in organic solvents, it reacts with water yielding ammonia and boric acid; with hydrogen chloride it forms a trihydrochloride and at 125°–130° decomposes into boron nitride and ammonia.

Boron Trifluoride, BF_3, may be prepared by heating a mixture of potassium fluoborate, KBF_4, and boric oxide with sulphuric acid; silicon fluoride which is always present as an impurity is greatly reduced in amount by passing the gas over boric oxide at 800° (O. Ruff, Z. anorg. Chem. 1932, **206**, 59). According to W. Biltz *et al.* (Z. anorg. Chem. 1932, **207**, 63) diazobenzene borofluoride, easily prepared from fluoboric acid and diazobenzene hydrochloride (Ber. 1927, **60**, 116, 1187), is a convenient source of pure boron trifluoride. The borofluoride is heated to 120° and the products of decomposition BF_3, C_6H_5F, and N_2 led into cooled receivers; C_6H_5F is condensed by carbon dioxide snow, and BF_3 by liquid air.

Boron fluoride is a colourless gas, fuming in moist air. A preparation containing less than 1·7% SiF_4 had the following properties: m.p. −128°, b.p. −101°/760 mm. (Ruff, *l.c.*; Moissan, Compt. rend. 1904, **139**, 711). It is rapidly absorbed and hydrolysed by water yielding fluoboric and boric acids. Boron trifluoride combines with ammonia, alcohols, ether, and acetone forming addition compounds; in reaction with organic substances it often behaves like aluminium chloride (H. Meerwein, Ber. 1933, **66**, [B], 411). For co-ordination compounds, *see* G. T. Morgan and R. Taylor (J.C.S. 1932, 1497). A method of manufacture from boric oxide, calcium fluoride, and sulphuric anhydride is given in U.S.P. 1865204, 28/6/32 (*cf.* Du Pont de Nemours, B.P. 463545, 30/3/37).

Boron Trichloride, BCl_3, can be prepared by passing a current of chlorine over a mixture of boric oxide and charcoal at a red heat, or in better yield if amorphous boron (H. V. A. Briscoe and P. L. Robinson, J.C.S. 1925, **127**, 696) or iron boride (J. Hoffmann, Z. anorg. Chem. 1910, **66**, 379) is substituted for the boric oxide and charcoal. The vapours are condensed in a freezing mixture, and the product purified by shaking with mercury and fractionation in a vacuum (A. Stock and E. Kuss, Ber. 1923, **56**,

[B], 1463). Boron trichloride is a colourless, very mobile, highly refractive liquid, fuming strongly in air, m p $-107°$, b p. 12 5°/760 mm (A. Stock and O. Priess, Ber 1914, 47, 3109), the density has been determined by Briscoe *et al* (J.C S. 1927, 282), average value at 11°, 1·3492, the differing values of the density of three specimens depend on the proportion of the isotopes in boron from three different sources, California, Tuscany, and Asia Minor (*v.* ISOTOPES) Boron trichloride reacts immediately with water, yielding boric and hydrochloric acids. It forms addition compounds, *e g* $BCl_3,POCl_3$, $BCl_3,12H_2S$, $BCl_3,4FeCl_3$ *Ethyl borate and hydrochloric acid result from* its action on alcohol. With ammonia at $-23°$ it gives boramide, at 0° borimide Boron trichloride has been claimed as a refrigerant in G.P. 574562.

Boron Tribromide, BBr_3, prepared by heating boron in bromine vapour, is a colourless, fuming liquid, m p. -46 0°, b p 90 1°/740 mm. (A. Stock and E. Kuss, Ber 1914, 47, 3114, 1923, 56, [B], 1463). It reacts violently with water, forms addition compounds with salts and esters, and resembles boron trichloride in its reaction with ammonia at low temperatures As a reagent containing boron it is more convenient than the trichloride as it can be purified from silicon compounds by distillation under ordinary pressure

Boron Triodide, BI_3—H Moissan (Compt *rend.* 1891, 112, 717; 1892, 114, 622) obtained the compound as a crystalline sublimate when hydrogen iodide was passed over strongly heated amorphous boron, prepared by the method of Deville and Wohler (sodium reduction of boric oxide), which contains borides of sodium and iron to which it owes its reactivity. Moissan's purified amorphous boron is useless for the purpose. Boron triodide forms colourless transparent crystals, m p 43°, b p 210°, it reacts violently with water forming hydriodic and boric acids

Metallic Borides.—According to L Hackspill (Helv. Chim. Acta, 1933, 16, 1118) boron combines with all the metals except gold, silver, and copper A number of borides have been described (*see* J W. Mellor, "*Inorganic* Chemistry," V, 1924, 23–32) and are usually prepared by heating the metal with amorphous boron, or with boric oxide, or in the vapour of boron trichloride.

Magnesium Boride, Mg_3B_2 (A. Stock *et al.*, Ber. 1912, 45, 3543; 1923, 56, [B], 790) has frequently been used as a source of boron hydrides. *Aluminium borides* have been mentioned under Crystalline Boron (*supra*, p. 36).

Technical *iron boride* (B 20%) and *manganese boride* (B 30–35%) are mixtures of several borides differing in their resistance to attack by chlorine and acids (J. Hoffmann, Z anorg. Chem 1910, 66, 394). These borides have been added to alloy steels to increase the hardness. L Andrieux (Ann. Chim. Phys. 1929, [x], 12, 423), by electrolysis of a mixture of the borate and fluoride of the metal, obtained CaB_6, SrB_6, BaB_6, and MnB. By employing a mixture of fluoride and borate of a metal of the alkalis or of the alkaline earths with the oxide of a metal of which the boride was required, he prepared CeB_6, LaB_6, NdB_6, GdB_6, YB_6, ErB_6, ThB_6, Zn_3B_4, TiB_2, VB_2, Cr_3B_2, UB_4, and MnB. According to B.P. 440764, 6/1/36, borides of metals other than alkali metals are obtained by the electrolysis of a molten bath of boric oxide and the chloride and/or oxide of the metal whose boride is to be prepared.

Zr_3B_4, VB, UB_2, and WB_2 were prepared by Tucker and Moody (J.C S. 1902, 81, 14), Wedekind (Ber 1913, 46, 1198) by heating the metals with boron in an electric vacuum furnace to 1,800°–2,200°. C. Agte and K. Moers (Z anorg Chem. 1931, 198, 233) prepared the borides of *Ti, Zr, Hf, V,* and Ta in small yield, but relatively pure, by a "growth" method, in which a tungsten wire is heated electrically to a high temperature in a mixture of the vapours of boron tribromide and of the metallic chloride, and hydrogen. The metallic boride is deposited on the wire. Tungsten boride melts at 3,195° abs, zirconium boride at 3,265° abs, hafnium boride at 3,335° abs. Their electrical conductivities are remarkably high, they conduct electricity better than the free metals Their hardness is greater than that of corundum (K. Becker, "Hochschmelzende Hartstoffe," Berlin, 1935, pp. 35, 36, 55, 57, 61).

Boron Carbides.—These are very hard crystalline substances of varying composition; products approximating to B_6C, B_4C, B_3C, and BC have been described as well as some of *intermediate composition.*

The Carbide B_6C.—A. Joly (Compt. rend. 1883, 97, 456) separated some crystals from the products of interaction of aluminium and boric oxide contained in a carbon crucible, which consisted of boron and carbon (15 7%) corresponding to B_6C, and had the density, at 17°, 2 542. H. Moissan (*ibid.* 1894, 118, 556) prepared this carbide by heating boron in a closed carbon crucible to a very high temperature, or in well defined crystals by fusing copper or silver with which boron and sugar charcoal had been previously mixed. After removing the metal with nitric acid and the excess of carbon by repeated treatments with nitric acid and potassium chlorate, and finally boiling the *residue with sulphuric acid*, brilliant black crystals were obtained of density 2 51. These were very brittle and so hard that they could be used for polishing diamonds. They take fire at 1,000° when heated in oxygen, but no carbon dioxide is evolved at 500°. They are not attacked by mineral acids or by hydrofluoric acid, but were analysed by fusion with potassium and sodium carbonates, acidifying the cold product and distilling off the boric acid with methyl alcohol on to a known weight of calcium oxide and weighing the boric oxide as calcium borate. Carbon was estimated by combustion with lead chromate. S. A. Tucker and H. J. W Bliss (J. Amer. Chem. Soc. 1906, 28, 605) made this carbide (82 8% B) by adding boric oxide through a hollow carbon electrode to petroleum coke contained in a graphite crucible which served as the other pole of an electric arc. Hard alloys containing B_6C have been made by F. Krupp A.-G. (B.P. 378484, 4/5/31).

The Carbide B_4C is the composition of a

commercial boron carbide described by R. B. Ridgway (Trans. Amer. Electrochem. Soc. 1934, 66, 177 ; U.S.P. 1897214, 1933). Boric oxide is heated with coke in an electric resistance furnace to 2,500°–2,600°, the melt contains a core of crystalline boride approximating to B_4C. Its properties are density 2·508–2·522, resistivity 20°, 9·445 ohms/cm.^{3} ; the coefficient of thermal expansion between 25° and 800° is $4{\cdot}5\times10^{-6}$; its hardness is intermediate between carborundum and diamond. It is not attacked by acids or by alkaline solutions, but when powdered and heated will oxidise rapidly in air. Moulded articles can be made of the carbide, which is used for nozzles for sand-blasting, for dies for wire drawing, as a substitute for jewel bearings, and for thread guides.

The Carbide B_3C.—A carbide corresponding to this composition has been made by E. Podszus (Z. anorg. Chem. 1933, **211**, 41) by heating to a very high temperature a mixture of boron nitride with sugar charcoal, placed between carbon electrodes. Large octahedra of B_6C are formed at the same time. B_3C is harder than B_6C (*cf.* B.P. 204337, Conv. 20/9/22, assigned to Hartstoff-Metall Akt. Ges.).

The Carbide BC was obtained by O. Mühlhaeuser (Z. anorg. Chem. 1894, **5**, 92) as black spherical masses, containing 51·2% C, by heating 100 parts of boric oxide with 160 parts of carbon in an electric furnace.

Silicon Borides, SiB_3 and SiB_6, hard black crystals, were made by heating the mixtures of the elements (H. Moissan, Compt. rend. 1900, **131**, 139).

Boron Sulphide, B_2S_3, may be prepared as a crystalline sublimate by passing sulphur vapour, entrained by hydrogen, over amorphous boron heated to 1,200° (H. Moissan, Compt. rend. 1892, **114**, 618 ; **115**, 203). Hydrogen sulphide mixed with hydrogen gives improved results at 1,500° (Costeanu, *ibid.* 1913, **157**, 934). J. Hoffmann's product, obtained by passing hydrogen sulphide over iron or manganese boride at 200°–300°, was a mixture in varying proportions of B_2S_3 with $B_2S_3{\cdot}H_2S$ (Z. anorg. Chem. 1910, **66**, 368). Boron trisulphide forms glistening white needles, and is also obtained as white amorphous, and as transparent vitreous, masses. It begins to melt at 310°, its density is 1·55 (Moissan). Water decomposes it giving hydrogen sulphide and boric acid.

Boron Hydrosulphide, $B_2S_3{\cdot}H_2S$ (boron sulphide thiohydrate), was prepared by A. Stock *et al.* (Ber. 1901, **34**, 399, 3039) by passing hydrogen sulphide for six days into a boiling solution of borontribromide dissolved in its own weight of carbon disulphide; the solution evaporated in vacuo left crystalline B_2S_3,H_2S, m.p. 120°, in a sealed tube. It loses H_2S slowly at ordinary temperatures, rapidly at 100° ; water reacts violently yielding H_2S and H_3BO_3.

Boron Oxides.—*Boron Sub-oxides.*—E. Weintraub considered that Moissan's amorphous boron contained boron sub-oxides, B_6O (Ind. Eng. Chem. 1911, 3, 299) or B_7O (Trans. Amer. Electrochem. Soc. 1909, **16**, 173). Their properties are those ascribed to Moissan's boron. H. H. Kahlenberg (Trans. Amer. Electrochem. Soc. 1925, **47**, 59) prepared Moissan's boron (of gross composition B_7O) which after boiling with 1% KOH solution washing and drying, gave analytical figures corresponding to B_5O. This was heated with gold chloride solution, in which boron dissolves while gold is deposited. The residue after removal of gold was a brown powder not attacked by hot hydrochloric or sulphuric acids. Its composition was represented by B_3O.

Boron Monoxide, BO.—The spectrum of BO has been studied by several authors for the purpose of calculating the proportion of the isotopes ^{10}BO and ^{11}BO and thus arriving at a value for the atomic weight of boron. The vapour of boron trichloride is passed into a current of active nitrogen containing the necessary trace of oxygen (A. Elliott, Proc. Phys. Soc. 1933, **45**, 627). The spectrum of a carbon arc fed with borax, contains lines between 3,600 and 7,000Å ascribed by Mulliken (Physical Rev. 1925, [ii], **25**, 259) to boron monoxide (W. Scheib, Z. Physik, 1930, **60**, 74).

B_2O_2 and B_4O_5.—M. W. Travers, N. M. Gupta, and R. C. Ray, in "Some Compounds of Boron, Oxygen, and Hydrogen," London, 1916, describe the preparation of two lower oxides of boron, B_2O_2 and B_4O_5, and of borohydrates which form salts with alkalis. Magnesium boride, Mg_3B_2, was first prepared by heating 2 parts of magnesium powder with 1 part of boric oxide in a current of hydrogen (Ray, J.C.S. 1914, **104**, 2162). The product was powdered and extracted with water. Provided the magnesium had been completely converted into boride, a solution was obtained which, when made strongly alkaline with ammonia, filtered, and evaporated, left a residue consisting mainly of B_2O_2. Its solution gives off hydrogen in contact with all surfaces, and is a powerful reducing agent precipitating red copper hydride from cupric salts, or, if concentrated, a precipitate containing copper and boron. The solution is believed to contain $H_6B_2O_2$, it evolves 4 atoms of hydrogen on treatment with acids, the other two hydrogen atoms are removable by iodine. By treating magnesium boride with dilute potassium hydroxide solution and evaporating the filtrate, Ray obtained crystalline $K_2B_2O_2H_4$ (J.C.S. 1922, **121**, 1090). The oxide, B_4O_6, contained in the residue from the evaporation of an ammoniacal extract of magnesium boride had previously been prepared (*ibid.* 1918, **113**, 803 ; *see also* Quart. J. Indian Chem. Soc. 1924, **1**, 125). It is very unstable and readily oxidised to boric acid.

$B_2(OH)_4$?—A. Stock *et al.* (Ber. 1925, **58** [B], 655) obtained a solution considered to contain this or another new —B : B— oxide by the action of water on B_2Cl_4, v.t. 0°/44 mm., prepared by reducing BCl_3 in a zinc arc.

Potassium Hypoborate, KH_3BO (A. Stock and E. Kuss, Ber. 1914, **47**, 810), was obtained as colourless crystals by shaking dihydrotetraborane, B_4H_{10} at 0° with a frozen 40% potassium hydroxide solution :

$$B_4H_{10}+4KOH=4KH_3BO+H_2$$

The aqueous solution of the salt when boiled or acidified gives off hydrogen, about 800 c.c. from 1 g. and yields boric acid. The solution does not absorb atmospheric oxygen although it is a powerful reducing agent, precipitating copper hydride from cupric sulphate solution and evolving hydrogen. Even a very dilute solution of the hypoborate precipitates black nickel boride, Ni_2B, from a nickelous sulphate solution (A. Stock, "Hydrides of Boron and Silicon," 1933, p. 145). When the salt is heated in a vacuum it loses water and hydrogen at 110°, and at 400°–450° metallic potassium distils over, while hydrogen is still evolved.

Boric Oxide, Boron Trioxide, Boric Anhydride, B_2O_3, is formed when boron is burnt in oxygen; in air some boron nitride is also produced. It is usually prepared by dehydrating boric acid by heating it to redness in a platinum crucible and pouring the clear melt on to platinum foil; it forms a very hard glassy mass, which rapidly absorbs water while being pulverised. A white friable mass, which is a more convenient form for subsequent operations, is obtained by slowly heating boric acid to 200°, avoiding fusion, in vacuo over phosphorus pentoxide. S. S. Cole and N. W. Taylor (J. Amer. Chem. Soc. 1934, 56, 1648; J. Amer. Ceram. Soc. 1935, 18, 55) prepared a previously unknown crystalline boric oxide by heating boric acid in vacuo to 225° for 400 hours. The X-ray pattern then showed about 12 sharp lines instead of the diffused 294° band of boric oxide glass. It has m.p. 294±1°, d^{25}, 1·805; n_D, 1·458. Boric acid glass has the d^{25} 1·844. These authors ascribe the erroneous m.ps. 577° and 1,300° recorded in the literature to the high viscosity of the glassy form. Briscoe, Robinson, and Stephenson (J.C.S. 1926, 77) found the mean density of pure fused boric oxide glass to be 1·7952; Californian B_2O_3 at 17·36°, 1·79711, Peruvian B_2O_3 at 19·25°, 1·79404, were the extreme values for B_2O_3 from six different sources. They remark (l.c. 78) that the commonly accepted value is 1·88. Mott (Trans. Amer. Electrochem. Soc. 1918, 34, 264) determined the b.p. by an approximate method to be 1,500° under atmospheric pressure. Wartenberg and Bosse (Z. chem. Apparatenk. 1922, 28, 384) stated that the boiling-point was not reached at 1,501° under 138 mm. pressure. Boric oxide is notably volatile at 1,000° according to Tiede and Birnbräuer (Z. anorg. Chem. 1914, 87, 129). Bedson and Williams (Ber. 1881, 14, 2554) measured the refractive index of boric acid glass at 15·8°, with the following results: $n_{H\alpha}$ 1·46245, $n_{H\beta}$ 1·47024, n_D 1·46427. While fused boric oxide glass is solidifying it cracks and emits light (Dumas). The linear coefficients ($\times 10^{-6}$) of thermal expansion of boric oxide are, at 10°, 14·40; 100°, 14·50; 200°, 15·3; 245°, 19; 250°, 205; 334°, 210. There is an abrupt increase at about 250° (M. Samsoen, Compt. rend. 1925, 181, 354).

Boric oxide reacts with water, with evolution of considerable heat, the mixture sometimes boiling:

$$B_2O_3+3H_2O=2H_3BO_3+16·8 \text{ kg. cal.}$$

(Berthelot, Ann. Chim. Phys. 1879 [v], 17, 133). The powdered oxide prepared by Walton and Rosenbaum (J. Amer. Chem. Soc. 1928, 50, 1648) is a rapid and efficient drying agent for gases until it contains 25% water. The reactions of boric oxide with sodium, potassium, magnesium, calcium and aluminium have been considered under *Preparation of Boron*, with carbon under *Boron Carbide*, with nitrogen and carbon under *Boron Nitride*, with carbon and chlorine under *Boron Trichloride*.

Boric oxide is not reduced by phosphorus; phosphorus pentoxide forms boron phosphate, BPO_4, and arsenic oxide yields $BAsO_4$. It dissolves in hot sulphuric acid to a very viscous solution, and forms double compounds with sulphur trioxide, B_2O_3,SO_3, and $B_2O_3,2SO_3$. Hydrogen fluoride converts the oxide into boron trifluoride BF_3, hydrofluoric acid dissolves it rapidly, yielding a solution of tetrafluoboric acid, HBF_4, and probably another fluoboric acid (Travers and Malaprade, Compt. rend. 1928, 187, 765). At a red heat boric oxide decomposes many inorganic salts, forming borates, while the acids or their decomposition products are volatilised, under the same conditions many oxides are dissolved in the fused boric oxide forming, in some cases, coloured glasses, but SiO_2, Al_2O_3, Cr_2O_3, SnO_2, MoO_2, UO_2, U_3O_8, ZrO_2, ThO_2, Y_2O_3, Er_2O_3 are insoluble up to 1,400°. Crystalline borates were prepared by Ouvrard (Compt. rend. 1900, 130, 172, 335; 1901, 132, 257) by fusing a mixture of a metallic oxide (CaO, SrO, BaO, CdO, ZnO, NiO, MnO) with boric oxide and acid potassium fluoride.

Highly phosphorescent substances, "boric acid phosphors," consist of boric oxide or of partly dehydrated boric acid, containing traces of organic substances, e.g. orthoboric acid heated to 170°, with from 0·0001% to 0·01% fluorescein (Shirov, 1931, A. 696; Tiede and Thimann, Ber. 1926, 59, [B], 1706; Tiede and Ragoss, Ber. 1923, 56, [B], 655). 1 g. of boric acid is mixed with a few drops of an alcoholic fluorescein solution and the mixture heated until it is almost completely fused but not completely dehydrated. After exposure to light the material will glow brightly for about two minutes.

Boric Acid, *Boracic Acid, Orthoboric Acid*, H_3BO_3, occurs in the steam of the Tuscan soffioni (v. *Occurrence*), from which it is recovered. It is manufactured from native borax or a borate mineral, such as rasorite,

$$Na_2B_4O_7,4H_2O;$$

ulexite, $NaCaB_5O_9,8H_2O$; colemanite, $Ca_2B_6O_{11},5H_2O$; and pandermite,

$$Ca_2B_{12}O_{22},9H_2O.$$

A solution of borax or a suspension of the ground minerals is digested with dilute sulphuric acid and steam is blown through the mixture. The calcium sulphate formed from the minerals last mentioned is filtered off, boric acid crystallises from the filtrate. Sodium bisulphate may be used instead of sulphuric acid (A. Kelly, B.P. 351810, 20/8/30). Sulphur dioxide is employed in U.S.P. 1642535, 13/9/27, Appl. 4/9/24). The boric acid is crystallised out at a temperature just above that at which sodium

sulphate begins to crystallise and a cycle of operations is then commenced (B.P. 294236, 7/6/28 of the American Potash and Chemical Corp.). Orthoboric acid is readily obtained by treating a solution of 3 parts borax in 12 parts hot water with 1 part sulphuric acid. On cooling boric acid separates out, and is purified by one or more recrystallisations from water. Boric acid forms white, translucent, shining scales which are unctuous to the touch, or triclinic crystals from solutions containing sulphuric acid. When heated to 107° it is converted into metaboric acid HBO_2, and into pyroboric acid $H_2B_4O_7$, at 140° (Nasini and Ageno, Gazzetta, 1911, 41 [i], 131). Above 184°, B_2O_3, *boric acid glass*, is formed.

Sborgi and Ferri (Atti R. Accad. Lincei, 1920, [v], **13**, 586) have published the following values of the solubility of boric acid in water:

Temperature °C.	g. H_3BO_3 per 100 g. solution.	Temperature °C.	g. H_3BO_3 per 100 g. solution.
0°	2·59	60°	12·88
10°	3·47	69°	15·58
21°	4·89	80°	19·10
31°	6·43	90°	23·94
40°	8·02	99·5°	28·09
50°	10·35		

Bock (Ann. Physik, 1887, **30**, 638) determined the sp.gr. and conductivity of boric acid solutions at 18°:

g. H_3BO_3 in 100 g. solution.	Specific gravity.	Conductivity $10^8 \times K$.
0·776	1·0029	0·0483
1·92	1·0073	0·1322
2·88	1·0109	0·2246
3·612	1·0131	0·3217

Boric acid in solution is one of the worst conductors; the distilled water used in preparing the solutions had at 20° $K \times 10^8$, 0·028. International Critical Tables III, 70 (1928), Gerlach (Z. anal. Chem. 1869, **8**, 245), give the following values for the density, 15°/4°, of boric acid solutions: 1% H_3BO_3, 1·0045; 2%, 1·0103; 3%, 1·0165. Myers (J.C.S. 1917, **111**, 178) found that the hydration of boron trioxide takes place in two stages, first to metaboric acid, HBO_2, and then to orthoboric acid. Menzel, Schulz, and Deckert (Z. anorg. Chem. 1934, **220**, 49) from vapour tension measurements and X-ray analysis of the system B_2O_3—H_2O, conclude that HBO_2 and H_3BO_3 are the only hydrates formed. Bezzi (Annali Chim. Appl. 1932, **22**, 713) found that orthoboric acid begins to be converted into the meta-acid at 50°, at 100° the meta-acid is stable and not volatile, ortho-acid is alone volatile in steam up to temperatures slightly above 100°. Anschütz and Riepenkröger (Ber. 1925, **58**, [B], 1734) considered that orthoboric acid dissociates into water and the meta-acid when the temperature is sufficiently high, and the latter acid then volatilises with steam. Nasini (Atti R. Accad. Lincei, 1926, [vi], **3**, 27) maintains that orthoboric acid distils in steam at reduced pressures if the temperature is not below 60°; at higher temperatures it volatilises even at the ordinary pressure. The loss sustained by evaporating an aqueous solution at 65° is 0·20% of the water evaporated (Nasini and Ageno, *ibid.* 1912, [v], **21**, ii, 125). H_3BO_3 is readily volatilised in the vapour of methyl alcohol even at room temperature, ethyl alcohol is less efficient (*cf.* 1936, A. 1062). Boric acid is soluble in glycerol 1 in 4 parts, and in alcohol 1 in 30 parts. Its solubility in water is increased by additions of glycerol, mannitol, tartaric acid and oxalic acid, and diminished by sulphuric, nitric, hydrochloric and acetic acids.

Boric acid has mild antiseptic properties, but does not destroy putrefactive bacteria although it inhibits their growth. Its use as a food preservative is no longer permitted in Great Britain. It is an ingredient of mouth washes, eye lotions and antiseptic dusting powders. A solution of boric acid or borax, but chiefly the latter, is used in the citrus industry for washing oranges prior to packing for shipment to distant markets, an enormous tonnage being treated per annum in the United States, thus greatly reducing the loss due to spoilage of the fruit by moulds (*cf.* "Borates," 1933, p. 11, Imperial Institute, London).

Boric acid has a marked tendency to form complex compounds, *e.g.* boroarsenites, borotungstates, boromolybdates, borovanadates, boromalates, borotartrates. Fox and Gauge (J.C.S. 1911, **99**, 1075) isolated mannitoboric acid, m.p. 89·5°, by means of the reaction $C_6H_{14}O_6 + H_3BO_3 - H_2O = C_6H_{15}O_8B$. The complex acids formed in mannitol and glycerol solutions are comparatively strong acids, of importance for analysis. For the manufacture of boric acid in Italy, *see Production* (p. 40).

Metaboric Acid, HBO_2 or $B_2O_3 \cdot H_2O$, is a product of dehydrating boric acid (*v. supra*). At 100° the tension of dissociation is 60 mm., becoming almost zero when the reaction

$$H_3BO_3 = HBO_2 + H_2O$$

is complete (Lescœur, Ann. Chim. Phys. 1890, [vi], **19**, 42). In moist air or in aqueous solution metaboric acid is converted, with measurable velocity, into orthoboric acid (Myers, J.C.S. 1917, **111**, 172).

Pyroboric Acid, Tetraboric Acid, $H_2B_4O_7$.—A residue corresponding to this composition has been obtained several times by dehydrating boric acid at 130° (Menzel *et al.*, *l.c.*) or at 140° (Nasini and Ageno, *l.c.*), but according to the first-named authors the product is a mixture of HBO_2 and B_2O_3. For the salts of this acid, *see Borates* (*infra*).

Metallic Borates.

Borates are obtained by the action of boric acid on metallic oxides or their salts, in solution or by fusion.

In solution boric acid is a very weak acid: a cold saturated aqueous solution colours litmus a wine-red; a hot saturated solution gives a bright red colour. It is expelled by almost all acids from its combinations, partially so even by

carbonic acid and hydrogen sulphide. A boiling concentrated solution, however, decomposes carbonates and soluble sulphides and manganese sulphide Hackspill, Rollett and Andrès (Compt. rend. 1931, 192, 48) heated mixtures of alkali chlorides with a large excess of boric acid in steam at 100°–150°, and found that after 30 minutes the hydrochloric acid was completely evolved, leaving a pentaborate, $M_2O,5B_2O_3$, except in the case of sodium chloride, when a chloroborate,

$$Na_2O\,5B_2O_3,NaCl,$$

is produced; whilst sodium nitrate yields a triborate, $Na_2O,3B_2O_3$.

At high temperatures, fused boric acid is capable of decomposing the salts of all more volatile acids.

The borates of the alkali metals are soluble in water, but precipitated by alcohol. The borates of the other metals are insoluble, or sparingly so in water Soluble borates produce precipitates in solutions of salts of calcium, barium, strontium, nickel and cobalt, and of ferric salts which are soluble in ammonium chloride.

Anhydrous borates are produced by fusing boric oxide at 1,350°–1,450° for 3 hours with the equivalent quantity of a metallic oxide (valency of metal atoms=valency of boron atoms). The oxides soluble in boric oxide form three groups (1) The oxides of lithium, potassium, sodium, rubidium, cæsium, thallium and silver produce clear fusions which either crystallise or leave clear glasses on cooling. (2) Cuprous oxide, and oxides of lead, bismuth, antimony, arsenic, titanium, molybdenum and tungsten produce clear fusions at high temperatures which form suspensions on cooling. (3) The oxides of calcium, strontium, barium, magnesium, zinc, cadmium, manganese, iron, cobalt and nickel do not give homogeneous fusions, but separate into two layers. Beryllium oxide, titanium dioxide, and silica are insoluble in fused boric oxide (W. Guertler, J.S.C I. 1908, 27, 158; Z anorg Chem. 1904, 40, 225)

Borates have also been prepared electrolytically by Levi and Castellani by electrolysing boric acid and an alkaline earth chloride in a divided cell (J S C I. 1909, 28, 248)

Ammonium borates.—*Laderellite*,

$$(NH_4)_2B_{10}O_{16},5H_2O,$$

occurs in the Tuscan lagoons in small crystalline rhomboidal plates (D'Achiardi, Chem. Soc. Abstr. 1900, 600). Of the eleven ammonium borates which had been described, U. Sborgi (Atti R. Accad. Lincei, 1912, [v], 21, ii, 855) obtained only one, viz. $(NH_4)_2O,5B_2O_3,8H_2O$, and, in addition, a new borate,

$$2(NH_4)_2O,4B_2O_3,5H_2O,$$

by keeping mixtures of ammonia, boric oxide, and water at 30° until equilibrium was obtained. At 60° the first named salt exists and also $(NH_4)_2O,4B_2O_3,6H_2O$, and

$$(NH_4)_2O,2B_2O_3,4H_2O$$

(*ibid.*, 1915, [v], 24, i, 1225; *cf.* Menzel, Z. anorg. Chem. 1927, 164, 22).

Barium borates.—The interaction of barium hydroxide and boric acid in aqueous solution has been studied by Sborgi (Atti R. Accad. Lincei, 1914, [v], 23, i, 530, 717, 854). The only stable compounds which appear to exist are the two triborates, $BaO,3B_2O_3,7H_2O$ and

$$2BaO,3B_2O_3,6H_2O,$$

and the metaborate $BaO,B_2O_3,4H_2O$.

Calcium borates.—Hydrated calcium borates occur as the important minerals colemanite, $Ca_2B_6O_{11},5H_2O$, and pandermite,

$$Ca_5B_{12}O_{23},9H_2O,$$

as mined, nearly similar to the Oregon mineral priceite $Ca_4B_{10}O_{19},7H_2O$. Sborgi (*ibid.* 1913, [v], 22, i, 798) prepared two borates stable in water at 30°,

$$CaO,B_2O_3,6H_2O \text{ and } 2CaO,3B_2O_3,9H_2O.$$

Copper borate, CuO,B_2O_3, blue crystals, is obtained by fusing cupric oxide with an excess of boric oxide, and has been proposed as a pigment, being used in the colouring of porcelain.

Lead borates.—By mixing concentrated solutions of lead nitrate and borax, the metaborate $Pb(BO_2)_2,H_2O$ is precipitated, and by the use of solutions of smaller concentrations Rose obtained many basic salts. They all melt on strong heating to colourless or light-yellow, highly refractive glasses, the hardness increasing with the boron content. Glasses may be obtained by fusing together lead oxide and boric acid in any proportions greater than 0 0725 equivalent of $3(PbO)$ to 1 equivalent B_2O_3, but below this limit a suspension is formed on cooling. (Guertler, Z. anorg Chem. 1904, 40, 227). Precipitated lead borate is used as a drier in boiled linseed oil and in mixed paints.

Magnesium chloro-borate is found in northern Germany as the crystalline mineral boracite (*q v.*), $6MgO,MgCl_2,8B_2O_3$, also described as $5MgO,MgCl_2,7B_2O_3$.

Manganese borate, a crystalline precipitate, $Mn_4H(BO_3)_3H_2O$, from mixed solutions of borax and manganous sulphate (Hartley and Ramage, J.C S 1893, 63, 129), is used as a paint drier.

Potassium borates.—Dukelski (Z. anorg. Chem. 1906, 50, 38; 1907, 54, 45) describes three salts stable at ordinary temperatures: $K_2O,B_2O_3,2\,5H_2O$; $K_2O,2B_2O_3,4H_2O$; $K_2O,5B_2O_3,4H_2O$. Rollet and Andrès (Compt. rend. 1930, 191, 567) prepared potassium pentaborate, $KB_5O_8,4H_2O$, by adding potassium chloride solution to one containing ammonia and boric acid in the proportions required for $(NH_4)B_5O_8$.

Sodium borates.—The only commercially important compounds are sodium diborate (*v. Borax*), the perborate and the metaborate $NaBO_2,4H_2O$.

Acid borates $Na_2O{\cdot}3B_2O_3$ and $Na_2O,4B_2O_3$, melting at 694° and 783° respectively, may be obtained by fusing mixtures of borax and boron trioxide (Ponomarev, Z. anorg. Chem. 1914, 89, 383).

Sodium Diborate, Borax, Sodium Tetraborate, $Na_2B_4O_7,10H_2O$ —Borax occurs in the crude state in what are termed borax marshes, which are generally the bottoms of dried up lakes, or, where tincal is found, lakes that are nearly dried. The crude borax in the former instances is found lying on the surface of the plain, of a

peculiar greyish-yellow colour, having a depth of from 1 in. to 18 in. It is generally associated with other substances, both soluble and insoluble, *e.g.* $NaCl$, Na_2SO_4, Na_2CO_3, $CaCO_3$, Al_2O_3, Fe_2O_3, sand.

Borax is now manufactured from *rasorite* (*kernite*), $Na_2B_4O_7,4H_2O$, which is the most important boron mineral, and is found in California. It was discovered in 1926, and on account of its composition and economical working, it has entirely replaced the other boron minerals in the manufacture of borax.

The crude mineral, as mined, consists of rasorite and gangue (shale and clay). The bulk of the latter is removed by mechanical means before despatching it from the mines. The process consists of crushing and grinding the freshly mined ore, which is then passed through an electro-magnetic separation plant. In this way the more magnetic part (shale) is separated to a great extent from the less magnetic part (rasorite). The mineral is further subjected to a current of air at about 130°C. in a rotary drier, whereby it loses part of its water of crystallisation. A product is finally obtained which is stable, fairly uniform, and contains about 45% B_2O_3.

The manufacture of borax from rasorite concentrates comprises several steps. The ore is treated first with hot water and/or mother liquor from a previous extraction, whereby borax goes into solution. If the solution contains dissolved silica, the latter should be rendered insoluble by adding a precipitating agent, after which the hot solution containing about 35–37% borax is filtered, the insoluble residue going to waste. The hot filtrate is diluted to a strength of 30–33% borax, and, if necessary, treated with an oxidising agent to destroy any colouring matter that may be present. A second filtration follows, and the borax is obtained from the resulting clear solution by crystallisation, which is carried out by cooling either slowly or rapidly. In the former case, crystallisation takes place in large iron tanks, the time for the solution to cool down being 5 or 6 days, and the product consisting of large, well-developed crystals.

By the second method, the hot solution enters a vessel equipped with an artificial cooling device and an automatic stirrer, by the use of which the borax is obtained in a granular form in from 3 to 5 hours. The granulated borax is separated from the mother liquors by centrifugal machines and finally dried in a special dryer using a current of hot air. Crystallisation under vacuum is also employed in the production of granulated borax from hot solutions.

Before the discovery of rasorite, borax was made exclusively from the calcium borate ores, colemanite and ulexite. These ores had to be concentrated by calcination and a separation process in order to increase their boron values. The manufacturing steps in the process of making borax from these minerals were similar to those used for rasorite. However, the cost of production from calcium borate minerals is much heavier than from rasorite, because the plant has to be larger and more elaborate. These ores have to be decomposed by means of soda ash and bicarbonate of soda (mostly under pressure) whereby sodium borate and calcium carbonate are formed at the same time; the latter goes to waste, but requires an extensive filter press installation. The handling of this large quantity of waste product usually presents difficulties and increases manufacturing costs. Evaporation of mother liquors which eventually become foul and run to waste is necessary when borate of lime, especially ulexite, has to be worked, the consequence being lower production and increased costs.

The increasing uses of borax for industrial purposes have been stimulated by the low prices of this product, which stand, in most countries, at levels lower than pre-war. This has been made possible by the discovery of rasorite, from which, for reasons stated above, borax can be manufactured much more cheaply than from the calcium borate ores formerly employed.

Properties.—Borax forms two varieties of crystals, (1) the *decahydrate*, which is produced by allowing solutions of borax to crystallise by cooling down to the ordinary temperature; (2) the so-called *octahedral borax* (actually hexagonal), a pentahydrate which separates out when the solution is allowed to crystallise above 62°.

(1) *Ordinary or prismatic borax*,

$$Na_2B_4O_7,10H_2O,$$

forms large transparent monoclinic prisms with truncated lateral edges. They effloresce when exposed to the air, have a rather sweet, cooling, alkaline taste, and a sp.gr. variously stated as 1·692–1·757. When heated they melt in their water of crystallisation, swell up, and leave a porous spongy mass, called burnt or calcined borax (*borax usta*), and fuse at a red heat to a colourless anhydrous glass (vitrified borax) with a sp.gr. of 2·36, which slowly absorbs water from the air, reforming prismatic borax. At 62° the decahydrate undergoes transition into the pentahydrate $Na_2B_4O_7,5H_2O$. At 130° the salt contains 3 mols. H_2O; at 150°, 2 mols. H_2O; at 180°, 1 mol. H_2O. At 318° it becomes anhydrous. At very low vapour pressures of water fresh borax passes irreversibly into an amorphous material with about $2H_2O$, which may be rehydrated to the pentahydrate. Anhydrous $Na_2B_4O_7$, m.p. 741°, crystallises rapidly at 600° (Menzel *et al.*, Z. anorg. Chem. 1935, 224, 1). $Na_2B_4O_7,4H_2O$ (*cf.* rasorite, *supra*) does not occur in the dehydration of higher hydrates. In vacuo at 60° borax quickly evolves 8 mols. of water (Kieffer, Compt. rend. 10e Congrès Chim. Ind. 1930, 520).

When borax is distilled with methyl alcohol, about 50% of the boric acid comes over fairly readily, and on longer treatment nearly 60%. From the liquor remaining in the flask, crystals of $NaBO_2,5CH_3{\cdot}OH$ separate (Polenske, Analyst, 1902, 27, 34).

Borax dissolves in water, but is insoluble in alcohol. The aqueous solution has an alkaline reaction, and changes the colour of an alcoholic solution of turmeric to brown; a small quantity of a mineral acid restores the original yellow

colour, but a larger quantity liberates boric acid in sufficient quantity to produce the characteristic brown coloration. Its solubility in water at different temperatures is shown in the following table:

SOLUBILITY OF BORAX IN WATER

°C.	Solid	g. $Na_2B_4O_7$ in 100 g solution
0 45	ice and $Na_2B_4O_7,10H_2O$	1·086 (1)
0	"	1·10 (2)
10	"	1 603 (2)
16	"	2·135 (2)
18	"	2 271 (3)
20	"	2 520 (1)
25	"	3 059 (3)
30	"	3·750 (1)
35	"	4 829 (4)
45	"	7·49 (4)
50	"	9 520 (4)
55	"	12 37 (4)
65	$Na_2B_4O_7,5H_2O$	17·953 (1)
80	"	23 9 (4)
102 9 (b p)	"	37 080 (4)

(1) U Sborgi and E Gallichi (Gazzetta, 1924, 54, 263)
(2) U Sborgi and Cesaroni (Atti Soc. Toscana, 30, 4, quoted in (1))
(3) H Menzel (Z anorg Chem. 1927, 166, 71)
(4) U Sborgi, E. Bovalini and L Capellini (Gazzetta, 1924, 54, 298).

For conditions determining the crystallisation of borax, see Levi and Castellani (Gazzetta, 1901, 40, i, 138).

At the temperature of 27 , borax solutions hold 1 lb of borax to the imperial gallon, and have a sp gr of 1 050, or 10° Tw The general crystallising strength is 1 160 sp gr , or 32° Tw., when the solution holds 5 lb. of borax to the gallon, crystallisation commencing at 65 5°.

The specific gravity at 15° of borax solutions (G T Gerlach, Z anal Chem. 1889, 28, 473) *is related to the concentration, as follows :*

Sp g	g Substance in 100 g Solution	
	$Na_2B_4O_7,10H_2O$	$Na_2B_4O_7$
1 0049	1	0 5288
1 0099	2	1 0576
1·0149	3	1 5864
1 0199	4	2·1152
1 0249	5	2 6439
1 0299	6	3 1727
1 032	supersaturated solution at 15°	

Borax is easily decomposed by acids. *Hydrochloric acid leaves, on evaporation,* sodium chloride and free boric acid *Carbonic acid* is absorbed from the air by a solution of borax, and no borax is precipitated on the addition of alcohol (Schweizer, Annalen, 1850, 76, 268) Saturated with *sulphuretted hydrogen* and mixed *with alcohol,* the liquid separates on the addition of ether into two layers, the lower containing sodium sulphide, the upper free boric acid (Schweizer, *l c.*). With *sodium fluoride* it forms sodium fluoroborate. When 1 part *tartaric* acid is mixed with 2 parts of a hot solution of borax, boric acid separates out on cooling. If the tartaric acid be increased, the separation of boric acid likewise increases up to a certain point, after which it diminishes, and ultimately is no longer separated. *Potassium hydrogen tartrate* forms a double salt with borax. *Silicic acid* is insoluble, or nearly so, in solutions of borax Cocaine and many alkaloids are precipitated by borax solution. Silver nitrate *precipitates white $AgBO_2$ from strong solutions* of borax, dilute solutions yield brown Ag_2O (Rose, Pogg Ann. 1852, 86, 470)

Benzoic, tartaric and gallic acids are more soluble in borax solution than in water. Many fatty acids and resins, notably shellac, dissolve as readily in borax as in alkaline leys, the borax behaving like a mixture of boric acid and free soda

Anhydrous borax fuses at 741° and readily dissolves and unites with metallic oxides, forming *a fusible glass of a double salt, which property* renders it of great use in soldering and in metallurgical operations and in blowpipe analysis, the glasses thus formed often exhibiting characteristic colours. It is used also in the preparation of easily fusible glass fluxes for enamels and glazes.

(2) *Octahedral borax,* $Na_2B_4O_7,5H_2O$, is obtained by allowing a saturated solution of borax to cool down to about 60° in a warm place and removing the crystals.

The crystals are regular, transparent octahedra, belonging to the hexagonal system, harder than the ordinary borax. They have a conchoidal fracture and a sp gr. of 1 8. They do not change in dry air, but absorb moisture very *readily and become turbid. At 116° they* decompose, passing into the dehydrate (Kieffer, Compt. rend , *10e Congrès Chim. Ind* 1930, 520). They fuse more readily than the prismatic crystals, and with less intumescence, and without decrepitating. Octahedral borax is therefore better adapted for soldering and as a flux than common borax, and the smaller quantity of water (a difference of 17%) diminishes the cost of transport. The prismatic variety is, however, generally preferred, probably because it is cheaper weight for weight.

Borax effloresces, so that the B.P. standard demands that the salt should not contain less than 99% or more than the equivalent of 103% of $Na_4B_2O_7,10H_2O$. Limit tests are specified for As, Pb, Cl, SO_4, and Fe In medicine it is used for lotions and hair washes. Powdered borax is used as an insecticide

Borax and boric acid are applied in the manufacturing industries as follows :

Abrasives—Boron carbide and silicon boride.

Adhesives and Distempers—Borax as a solvent in the preparation of casein glues, distempers, etc.

Brick and Tile Makers—Glazed surfaces.

Candle Makers.—Preparation of wicks.

Cement.—Making the finest kinds, which take a polish.

China and Earthenware.—In preparing a frit used for the glazing of pottery of all descriptions.

Colour Makers.—In preparing Guignet's green and manganese borate.

Coppersmiths.—In brazing.

Electroplating.—Addition of boric acid to the bath for Ni, Cr, Zn and Sn plating, sodium perborate in Sn plating.

Enamelled Iron.—In enamelled coatings to cast and wrought iron.

Glass.—Borosilicate heat-resisting, chemically-resistant and optical glasses ; also as a flux in the production of ordinary blown, pressed or drawn glass ware.

Hat Makers.—Dissolving shellac in borax solution to prepare a stiffener.

Jewellers.—As a flux in soldering.

Laundry.—Borax in starch-glaze ; sodium perborate in washing powders.

Manufacturing Chemistry.—Boric acid addition to the sulphuric acid for sulphonation and for washing crude benzol.

Metallurgy.—Very hard alloys containing boron. Deoxidising copper with calcium boride.

Paper Making.—In coated paper or board.

Preservatives.—Permitted use of borax and boric acid in some countries but not in Great Britain.

Safe Makers.—Lining for safes to resist fire.

Tanning.—Soaking and de-liming hides, and in leather-dressing.

Textiles.—Bleaching, mordanting, fireproofing.

Sodium Metaborate.—The metaborate of commerce is $NaBO_2,4H_2O$, which tends to become covered with a white powder when exposed to the air. On heating in an enclosed space it melts in its crystal water at 53·5°C. At higher temperatures it loses all its water, the anhydrous salt melting at 965°C. It is soluble to the extent of 33·5 parts per 100 parts of water at 19°C. The density of aqueous solutions of sodium metaborate is, according to International Critical Tables, 3, 86, as follows :

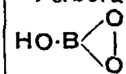
Wt. % of $NaBO_2$	d_4^{20}
1	1·0089
2	1·0198
4	1·0417
6	1·0640
8	1·0866
10	1·1095
12	1·1327

The solubility in water increases rapidly with the temperature.

Temperature °C.	Solubility per cent.
32·2	53·5
37·7	59
43·3	65·5
48·8	73
54·4	81

A method of preparing the salt in large crystals is given by Menzel, Z. anorg. Chem. 1927, 166, 68. It is used in the following industries : (1) photography, for production of fine-grain developers ; (2) adhesives, as a solvent for casein ; (3) cosmetics, for preparation of bath salts.

Perborates are salts of the acid HBO_3 or



which has not been prepared in the free state on account of its instability. The alkali and alkaline earth salts are soluble in water and have an alkaline reaction. They behave in solution like mixtures of borates with hydrogen peroxide ; the active oxygen being liberated by heat, by acidifying the solution or by large dilution. Oxydases, reductases and manganese dioxide cause them to give up the whole of their reactive oxygen. They convert chromic acid into perchromic acid and molybdates into yellow permolybdates. They readily oxidise protoxides and their salts into higher oxides, but do not always form perborates. Ferrous, mercurous, manganous and lead salts yield higher oxides ; the salts of other metals yield perborates of an indefinite or basic composition. Perborates of the alkali metals may be obtained by careful precipitation of solutions of alkali borates with alcohol in the presence of hydrogen peroxide.

Ammonium perborate, $NH_4BO_3,\frac{1}{2}H_2O$ (Tanatar, Z. physikal. Chem. 1898, 26, 133), is the best characterised of the several perborates resulting from the action of ammonia and hydrogen peroxide on ammonium borate. It contains 16·34–16·41% of active oxygen.

Potassium perborate, $KBO_3,\frac{1}{2}H_2O$, is obtained by the action of hydrogen peroxide on potassium borate.

Sodium perborate, $NaBO_3,4H_2O$. When 248 g. of boric acid are mixed with 78 g. of sodium peroxide and added gradually to 2 litres of cold water, a clear solution is formed from which a crystalline substance separates out in 90% yield. This substance, which has the composition $Na_2B_4O_8,10H_2O$, is called *perborax,* and is soluble in water to the extent of 42 g. per litre at 11°. When one-half of its sodium is displaced by addition of hydrochloric acid to the solution, a crystalline *sodium perborate* is precipitated. This is a stable substance, containing 10·38% active oxygen, and can be preserved indefinitely at ordinary temperatures. It dissolves readily with slight decomposition in water at 50°–60°, and a vigorous ebullition of oxygen takes place at 100°. The solubility of sodium perborate in water was determined by Jaubert (Rev. gén. Chim. pure appl. 1905, [vii], 8, 163 ; Chem. Zentr. 1905, ii, 99) ; expressed as g. $NaBO_3,4H_2O$ per litre of water, the figures are : 15°, 25·5 g. ; 21°, 26·9 g. ; 26°, 28·5 g. ; 32°, 37·8 g. The cold aqueous solution possesses all the properties of hydrogen peroxide. When powdered sodium perborate is added gradually to its equivalent of 50% sulphuric acid, and the solution filtered through gun-cotton, a very strong (150–200 vols.) solution of hydrogen peroxide is obtained. With cold concentrated sulphuric acid the mixture decom-

poses, evolving oxygen containing ozone (Dubois, Compt. rend. 1905, 140, 506).

Sodium perborate is largely used as an ingredient of washing powders, in which it acts as a bleaching agent and detergent. It has also found application in deodorants, dentifrices and antiseptics. The method of manufacture is either one depending on the employment of hydrogen peroxide, or it is electrolytic. According to the first method, a mixture of borax and crystallised sodium carbonate is treated with hydrogen peroxide when carbon dioxide is evolved and sodium perborate separates in coarse crystals (G P. 237608) The numerous British patents claiming electrolytic methods include 100152, 100153, 101620, 102089, 102359, 106460, all of 1916. K Ardnt (Z Electrochem. 1916, 22, 63; 1922, 28, 263) employed a tubular tin cathode cooled by a current of water and a platinum gauze anode in a bath containing 120 g sodium carbonate and 30 g. borax per litre, with additions of 0 5 g. sodium chromate and 1 drop of Turkey red oil The bath temperature was 14°–16° and the current density 10–20 amperes per sq. dcm A mixture of borax, sodium carbonate and sodium bicarbonate is added at intervals to reduce the proportion of caustic alkali formed in the bath. Percarbonate is the primary product of the electrolysis and this reacts with the borax forming perborate.

The percentage of active oxygen in sodium perborate is determined by titrating its solution in dilute sulphuric acid with 0 1*N*-potassium permanganate. The commercial salt contains from 9 5–10% active oxygen.

The constitution of the alkali perborates is disputed, Kretzschmar (Z. anorg Chem. 1934, 219, 17) and Menzel (*ibid.*, *idem.* 37) consider these salts to be substitution compounds of hydrogen peroxide. Krauss and Oettner (*ibid.* 1934, 218, 21) regard them as addition compounds and write the formula of sodium perborate, $Na_2B_2O_4,2H_2O_2\,6H_2O$.

Detection and Estimation of Boron.

Boron almost always occurs in the form of borates. When boric acid is in the free state it can readily be recognised by the green colour which it gives to the flame, and by its action upon turmeric.

Turmeric paper, when moistened with a solution of boric acid and dried, acquires a cherry-red colour which is not altered by dilute hydrochloric acid and is changed to bluish-black by a drop of sodium carbonate solution. The use of a viscose silk thread soaked in turmeric solution and dried, instead of paper, is an improvement (Chamot and Cole, Ind. Eng. Chem. 1918, 10, 48). Cassal and Gerrans (Chem. News, 1903, 87, 27) find that the sensitiveness is greatly increased if the paper is first moistened with 5% oxalic acid solution, and base a colorimetric method of estimation of boric acid on this method. Tananaev and Kulska (Ukrain. Chem. J. 1934, 9, 1) state that 0 001 mg. boron may be detected by this test (*cf.* Bertrand and Agulhon, Compt. rend. 1913, 157, 1433). The turmeric reaction is discussed with many references in Rüdisüli, "Nachweis, Bestimmung und Trennung der chemischen Elemente," 1923, vi, i, 1. To detect 0 001 mg. of boric acid per c c, the paper should be dried at the ordinary temperature (Low, J. Amer. Chem. Soc. 1906, 28, 807).

The green colour imparted to flame is a very delicate test for boron. It is, however, to be noted that salts of copper, barium and thallium also give a green coloration to the flame. When the boric acid is combined with a base the compound in the state of powder is decomposed by means of sulphuric acid, and the boric acid extracted by distilling with methyl alcohol, the test being applied to the distillate. Compounds not decomposed by sulphuric acid are fused with potash and digested with methyl alcohol and sulphuric acid.

A mixture of borax and methyl alcohol yields a green coloured flame if ignited, but with ethyl alcohol the presence of a mineral acid is necessary, 5% of methyl alcohol in ethyl alcohol may be detected by this means (Pieszczek, Pharm. Ztg. 1913, 58, 850). According to Stahl (Z. anal. Chem. 1931, 83, 340; 1935, 101, 342) the optimum mixture is sulphuric acid 3 c.c., methyl alcohol 15 c.c. The substance to be tested is mixed with 0 5 c c. of the freshly prepared mixture and allowed to stand in Rosenbladt's apparatus (*ibid.* 1887, 27, 19) for 15 minutes. The tube is then held for 30 seconds in a waterbath at 65° and a current of air passed through it into a non-luminous flat gas flame 0 5–1 cm. high. If the test is made in semi darkness 0 00076 mg. boron may be detected. In its quantitative form equal currents of air are passed simultaneously through the unknown and a standard boric acid solution into non-luminous flames of porcelain micro burners The concentration of the standard solution is varied until it gives the same intensity of flame coloration (Stahl, *ibid.* 83, 268, 1935, 101, 348). Glass and other insoluble substances are fused with sodium carbonate, followed by solution in hydrochloric acid, addition of methyl alcohol, boiling, and placing wet turmeric paper in the vapour (Tananaev and Kulska, *l.c.*).

Spot Test for Boric Acid—The reagent is *p* nitrobenzeneazochromotropic acid (Chromotrope 2B), by means of which 0 00008 mg. B in 1 . 500,000 dilution can be detected. Special precautions must be taken if oxidising anions or fluorides are present (Komarovsky and Poluektov, Mikrochem. 1934, 14, 317). F. Hahn (Compt. rend. 1933, 197, 762) neutralises the test solution to the green colour of bromothymol blue, neutral mannitol is then added to one half of the solution, and drops from each half are compared on a white tile. A yellowish green colour of the test solution is visible if the boron present exceeds 0 00002 mg. per c.c.

The gravimetric estimation of boron is difficult as there are no borates forming sufficiently insoluble precipitates of definite composition. The most reliable method is due to Gooch. If the boron is not present as boric acid, it is brought into that state by heating the sample with 20% or concentrated nitric acid, depending on the violence of the reaction, or if necessary the substance is heated with nitric acid for some

hours in a sealed tube. The resulting solution is repeatedly distilled with methyl alcohol, the boric acid passing over in the vapour. The distillate is then treated with an exactly weighed excess of pure lime, transferred to a platinum crucible, evaporated to dryness on the water bath and strongly heated. The increase in weight represents the boric anhydride (Moissan, Compt. rend. 1893, **116**, 1087).

The volumetric method is now generally used. It depends upon the fact that boric acid has no action on methyl orange but may be accurately titrated with caustic alkali, using phenol phthalein as indicator, provided the titrated solution contains a sufficiently large amount of glycerol—about one-half of its volume (Thomson, J.S.C.I. 1894, **13**, 432) or mannitol—10 g. per 100 c.c. (Foote, Ind. Eng. Chem. [Anal.], 1932, **4**, 38; Andrieux, Ann. Chim. 1929, [x], **12**, 432). The first step in the process is to obtain the boron in the form of boric acid or of a borate soluble in sulphuric acid. The whole of the boric acid present may then be distilled off by repeated distillations with methyl alcohol in presence of sulphuric acid. Excess of sodium hydroxide is added to the distillate, which is evaporated to dryness, and the residue dissolved in water. An excess of hydrochloric acid is then added and the liquid boiled under reflux to expel carbon dioxide. The excess of hydrochloric acid may be removed either by adding a solution of potassium iodide and potassium iodate and the liberated iodine being converted into iodide with 0·1*N*-thiosulphate; or by neutralising directly to methyl orange; mannitol or glycerol, of known neutral reaction, is then added in the quantities already indicated, and the solution titrated with 0·1*N*-sodium hydroxide in presence of phenol phthalein. The alkali must be free from carbonate. The method in use in the Government laboratory is described in Analyst, 1923, **48**, 416, and an alternative method, in presence of phosphoric acid, was devised by Monier-Williams (*ibid.*, *idem.* 413). The whole of the combined base in the borates of the alkalis and alkaline earths may be titrated with standard hydrochloric acid in the presence of methyl orange. Chemical glassware may contain boron, and the amount of contamination from this source is of importance in delicate work, *e.g.* biochemical effects of boron.

Reaction between Boric Acid and Sugars.—F. J. Berenstein (Biochem. Z. 1929, **215**, 344) observed that when boric acid and lævulose are mixed, hydrogen ions are liberated. Whereas in the titration of boric acid with sodium hydroxide using phenol phthalein as indicator only 10% of the acid is neutralised at the colour change, in the presence of sufficient galactose, 40%, of dextrose and lactose, 25%, but of lævulose (as with mannitol and glycerol), 100% of the acid is neutralised (*cf.* Hermans, Z. anorg. Chem. 1925, **142**, 83). J. N. G.

BORONATROCALCITE. An early name (G. L. Ulex, 1849) for the mineral ulexite, a hydrated borate of sodium and calcium,

$$NaCaB_5O_9,8H_2O$$

Most of the natural borates exported from South America (Chile, Bolivia, and Argentina) are of this species; it is also abundant in the borate deposits of California and Nevada. L. J. S.

BOROVERTIN. Trade name for hexamethylenetetramine borate,

$$C_6H_{12}N_4(H_3BO_3)_3,$$

a white powder, prescribed as a urinary antiseptic.

BORSALYL. Trade name for sodium borosalicylate.

BORT (BOART) *v.* ABRASIVES.

BORYL. Trade name for ethyl borosalicylate. Prepared by boiling together solutions of boric acid and salicylic acid and esterifying by the addition of alcohol and sulphuric acid. Needle-shaped crystals. Used in medicine as a substitute for ethyl salicylate (Monteil, J.S.C.I. 1908, **27**, 354).

"BOSA", a fermented beverage made from millet.

BOSCH. An inferior butter prepared in Holland. The term is sometimes used as synonymous with margarine.

BOSTONITE. A trade name formerly in use for the Canadian serpentine-asbestos (*v.* ASBESTOS). L. J. S.

BOSWELLINIC ACID. This dicarboxylic acid, $C_{32}H_{52}O_4$ (?), m.p. 150°–151°, obtained from olibanum, is in all probability a hydropicene triterpene since it gives sapotalin (1:2:7-trimethylnaphthalene) on selenium dehydrogenation (Beaucourt, Monatsh. 1929, **53–54**, 897; 1930, **55**, 185; Ruzicka, Brüngger, Egli, Ehmann, Furter and Hösli, Helv. Chim. Acta, 1932, **15**, 431). F. S. S.

BOTANY BAY GUM *v.* BALSAMS, Xanthorrhœa.

BOTRYOLITE *v.* CALCIUM, Silicoborate.

BOTTLE-NOSE OIL (ARCTIC SPERM OIL) is the oil—or, more strictly, the liquid wax—obtained from the head-cavity and blubber of the bottle-nose whales *Hyperoōdon rostratus* and *H. diodon* (*bidens*); it closely resembles sperm oil but on account of its greater tendency to "gum" commands a lower price than sperm oil (*cf.* Dunlop, J.S.C.I. 1908, **27**, 63; Tsujimoto, J. Soc. Chem. Ind. Japan, 1923, **26**, 209 (27 Supp.); Chem. Umschau, 1925, **32**, 127). E. L.

BOUILLON NOIR. A mixture of ferrous and ferric acetates employed as a mordant.

BOULANGERITE. A sulphantimonite, $5PbS,Sb_2S_3$.

BOURNONITE. Sulphantimonite of copper and lead $CuPbSbS_3$, crystallising as tabular orthorhombic crystals; these are frequently twinned and show re-entrant angles at the edges, hence the names "cogwheel-ore" and "wheel-ore." It is found in Cornwall, Harz, Bolivia, etc. It sometimes occurs in sufficient abundance to be used as an ore of copper and lead. L. J. S.

BOVEY COAL. A lignite or brown coal with a slaty cleavage.

BOWL METAL *v.* ANTIMONY.

BRAGA. An alcoholic beverage with a somewhat sweet taste, used in Roumania and prepared by the fermentation of millet. The seed is boiled with about twelve times its weight of water for 14 hours, the resulting viscous mass

cooled, stirred with water and allowed to ferment. The liquid is filtered and mixed with water to reduce the alcoholic strength to about 1·3% by weight, equivalent to 2·8% of proof spirit.

F. G. H. T.

BRAGGITE. (Pt,Pd,Ni)S, containing about 20% Pd and 5% Ni. This mineral was isolated as minute grains from the concentrates of the platinum bearing norite of the Bushveld, Transvaal, and being the first new mineral to be discovered by X ray methods it was named after Sir William H. Bragg and W. L. Bragg. The crystals are tetragonal with unit-cell dimensions a 6·37Å, c 6·58Å. *Cf.* cooperite (F. A. Bannister, Min. Mag. 1932, 23, 198).

L. J. S.

BRAIN LIPOID. *Impure Cephalin.* An extract of ox brain used for accelerating the coagulation of blood.

BRAN. The name given to the coarser fragments, consisting mainly of the outer layers of the seed coat, which are produced during the grinding or milling of cereal or other seeds. When the term is used without any descriptive adjective, the product from wheat is usually understood, but maize (corn), millet, barley, oats, buckwheat, rye, rice, and even peas and earth nuts yield products which are described as "bran." In the following discussion most attention is devoted to wheat bran, since this is the most important bran in Great Britain.

A very complete account of the microscopic structure of the various cereals and nuts is to be found in A. L. and K. B. Winton's "The Structure and Composition of Foods," Vol. I (John Wiley and Sons, New York, 1932). Bran is mainly derived from the pericarp and seedcoat, together with some adhering endosperm, and a smaller or larger content of germ, depending upon the efficiency of the milling process; in addition, the aleurone layer also remains with the bran after milling.

Table 1 supplies data as to the embryo, endosperm, and bran contents of the wheat grain.

TABLE 1.

Reference	Type of Wheat.	Endosperm	Embryo	Bran
		%	%	%
Fleurent, Compt. rend. 1896, 123, 327 (Bailey, "The Chemistry of Wheat Flour," p. 123, N.Y. Chem. Cat. Co., 1925).	Russian	84·95	2·00	13·05
	Algerian	84·99	1·50	13·51
	Canadian	84·94	2·05	13·01
Girard, "Le Froment et Sa Mouture," p. 28, Gauthier-Villars, 1903	Australian	83·82	1·41	14·77
	Polish	84·17	1·38	14·45
	French	85·08	1·48	13·44
	French	85·17	1·57	13·26
Bruère, J. Pharm. Chim. 1931, 14, 5	Not stated	83	1·4	15·6

The thickness of the hull of the grain varies considerably, even within one and the same variety (Hopf, Muhlenlab. 1935, 72, 69).

According to Temi (Mohs and Bruckner; Vol. I of Hoffmann-Mohs: "Das Getreidekorn," Paul Parey, Berlin, 2nd ed., 1931, pp. 237–238), however, the thickness of the hull, including the aleurone layer, amounts in the case of wheat to 110–120μ, and in rye to 95–100μ.

According to Hopf (*l.c.*) and Mohs and Bruckner (*l.c.*) there is as yet no practicable method for the accurate determination of the bran content of grain, but the following methods have recently been described: Schmorl (Pflanzenbau, 1933, 9, 313) describes the "Support" apparatus for washing out the other constituents of the grain; Hopf (*l.c.*) suggests two methods which yield approximate results: (1) based on determination of the ash content, and (2) by washing out the bran snips from an aqueous suspension of finely ground meal; Lowig (Z. ges. Getreide., Muhlen.- u. Bäckerew. 1935, 22, 31) suggests effecting the disintegration and dissolution of the contents of the grain by germination, the products being separated by squeezing and washing over a sieve.

Lack of space precludes a description of the flour milling process from which bran is obtained as a by-product. The reader is referred to P. A. Amos's "Processes of Flour Manufacture" (Longmans, Green & Co., London, 2nd ed., 1925) for a description of the English system, and to W. H. Strowd's "Commercial Feeds" (National Miller, Chicago, 2nd ed., 1925) for a brief outline of flour milling in relation to the production of bran in the U.S. An account of the milling of buckwheat is to be found in "Buckwheat Milling and its By-Products" (M. R. Coe, U.S. Dept. Agric. 1931, Circ. 190), and of rice milling in "The By-Products of Rice Milling" (J. B. Reed, U.S. Dept. Agric. 1917, Bull. 570).

Below are given some references to literature on the milling of other cereals: *Oats*—Lässer, Mühlenlab. 1932, 69, 905, 927 and 961; Milling, 1933, 80, 340; Ager, Nat. Amer. Miller, 1932, 60 (10), 16; Milling, 1932, 79, 458; Brückner and Dietz, Z. ges. Getreide-, Muhlen- u. Bäckerew. 1932, 19, 59, 76; Milling, 1934, 82, 594. *Barley*—Milling, 1934, 83, 240. *Rye*—Milling, 1934, 83, 10; Brown, Nat. Miller, 1925, 30 (12), 31.

Brief accounts of the manufacture, packing, handling, storage and loading of bran, with a view to ensuring its keeping qualities, are to be found in the Bull. Assoc. Oper. Millers, 1925, pp. 164 and 167, and 1932, p. 453, and in The

Miller, 1925, **50**, 946. There are very few data in chemical or milling literature concerning the spoiling of bran, but it is usually assumed that the heating of bran occurs in three stages. In the first place the respiration of the cells of damp bran leads to a rise in temperature sufficient to allow micro-organisms to develop. Their activity raises the temperature to about 70°C., at which point the absorption of oxygen would proceed at a greatly increased rate, sufficient to bring the temperature up to 150°C., when the bran would ignite spontaneously. Maurizio in his "Nahrungsmittel aus Getreide," Vol. I, p. 224 (Berlin: Paul Parey, 2nd ed., 1924) supplies such an explanation, and also discusses other aspects of the problem (*see also* Thaysen and Galloway "The Microbiology of Starch and Sugars," Oxford Univ. Press, 1930, p. 196; Chitty, Milling, 1934, **83**, 214; Hoffmann, Woch. Brau. 1897, Nos. 35–37; Z. physikal. Chem. 1898, **25**; Z. angew. Chem. 1902, No. 33; Versuchs-Kornhaus, Berlin, 1904, p. 212, etc.; Marienhagen, "Selbsterwärmung," p. 254).

Marchardier and Goujon (Ann. Falsif. 1914, **7**, 77) investigated the increase in the acidity of bran on spoilage; a normal bran contains less than 0·15% of acid, calculated as sulphuric acid. If 0·15–0·3% be present, the feed, while probably not dangerous, is undergoing decomposition, and all samples containing more than 0·3% should be condemned as unfit for food.

Varga (Arch. Chem. Mikros. **6**, 342; Amer. Chem. Abs. 1914, **8**, 380) describes a method of estimating mould spores in bran.

Some methods of treating bran to prevent deterioration are suggested in the article in The Miller, 1925, **50**, 946. Klug (Mühlenlab. 1933, **70**, 699) suggests briquetting the bran as a means of reducing (by 60%) the risk of decomposition during storage. Other methods of preservation are dealt with in Schiff-Giorgini (B.P. 205466); Woodlands, Ltd., Kent-Jones, and Amos (B.P. 378548); Legendre (B.P. 310980), Recherches et Inventions, 1927, No. 160, 445; 1929, **10**, 69; Compt. rend. 1927, **185**, 1156; and "Les Céréales": Armand Colin, Paris, 1935. An article by West and Cruz (Philippine J. Sci. 1933, **52**, 1) deals with the preservation of rice bran.

The analytical methods used for the examination of bran are in general the same as those used for the analysis of feeding stuffs. Since even a brief outline of such methods would occupy too much space, the reader is referred to the following standard publications on these subjects: "Cereal Laboratory Methods" (Amer. Assoc. Cereal Chemists, Omaha, Nebraska, 3rd ed., 1935); "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists" (Washington D.C., 3rd ed., 1931); the various volumes of the J. Assoc. Off. Agric. Chem.; The Fertilisers and Feeding Stuffs Act Regulations.

The following is a list of articles dealing with the analysis of milling products:

(*a*) *General.*—Coleman, Cereal Chem. 1927, **4**, 311; *ibid.* 1928, **5**, 269; König, Z. Unters. Lebensm. 1930, **59**, 564; Hertwig, J. Assoc. Off. Agric. Chem. 1923, **7**, 68; Hertwig and Palmore, *ibid.* 1923, **7**, 170. (*b*) *Adulteration.*—*See* discussion on "Adulteration," below. (*c*) *Ash.*—Nuret, "Les Matières Minérales: Les Cendres," Études sur la Meunerie (École Française de Meunerie Paris, 1932, p. 27ff.); Otterström, Suomen Kem. 1934, **7**, 76; (1934, B. 904); Simon, "The Physical Science of Flour Milling" (Liverpool: The Northern Publishing Co. 1930, pp. 125 and 219); (phosphoric acid) Lepper, Landw. Versuchs-Stat. 1930, **111**, 159. (*d*) *Fibre.*—Bidwell and Bopst, J. Assoc. Off. Agric. Chem. 1921, **5**, 58; Fisher and Carter, J.S.C.I. 1934, **53**, 313T; Forbes and Mensching, Ind. Eng. Chem. 1913, **5**, 258; Francis, J. Assoc. Off. Agric. Chem. 1920, **4**, 39; Fraps, *ibid.* 1923, **6**, 333; Haigh, *ibid.* 1921, **4**, 336; Hanson, *ibid.* 1924, **7**, 335; Korfhage, Minn. State Dairy and Food Comm., Div. Feed Insp. Ann. Rpt., 1922, **4**, 32; Lepper, Chem.-Ztg. 1926, **50**, 211; Scharrer and Kürschner, Bied. Zentr. 1931, B, **3**, 302. (*e*) *Lignin.*—Phillips, J. Assoc. Off. Agric. Chem. 1934, **17**, 277. (*f*) *Moisture.*—Bopst *et al.*, *ibid.* 1925, **8**, 354; Bunzell, Cereal Chem. 1935, **12**, 54; Clarke, J. Assoc. Off. Agric. Chem. 1920, **4**, 48; Coleman and Dixon, Cereal Chem. 1926, **3**, 419; Darkis, J. Assoc. Off. Agric. Chem. 1927, **10**, 178; Durham, Nat. Amer. Miller, 1934, **62**, (5), 59; Edlefsen, Agric. Eng. 1933, **14**, 243; Grattan, J. Assoc. Off. Agric. Chem. 1934, **17**, 178; Fisher and Thomlinson, J.S.C.I. 1932, **51**, 355T; Haltmeier, Mühlenlab. 1934, **71**, 1299; Swanson, N. W. Miller, 1934, **180**, 12 (Oct. 10); Weber, Wochbl. Papierfabr. 1925, **56**, 357. (*g*) *Nitrogen.*—Jones, U.S. Dept. Agric. 1931, Circ. 183; Markley and Hann, J. Assoc. Off. Agric. Chem. 1925, **8**, 455; Sandstedt, Cereal Chem. 1932, **9**, 156. (*h*) *Sand.*—Lepper, Landw. Versuchs-Stat. 1930, **110**, 305; Rüb, Chem.-Ztg. 1931, **55**, 221. (*i*) *Starch.*—Alpers and Ziegenspeck, Z. Nahr. Genussm. 1923, **45**, 163; Fraps, J. Assoc. Off. Agric. Chem. 1932, **15**, 304; Hopkins, Canad. J. Res. 1934, **11**, 751; Scheele and Svensson, Tekn. Tidskr. Kemi, **58**, 57 and 75 (Z. Unters. Lebensm. 1932, **63**, 343). (*j*) *Fat.*—Herd and Amos, Cereal Chem. 1930, **7**, 251.

The analyses of bran vary within wide limits. Some of the factors which contribute towards these variations are (1) the kind of wheat used; (2) the climatic conditions under which the wheat is grown; (3) the milling process used; (4) the composition of the grist; (5) the percentage of screenings incorporated; (6) the percentage of flour extracted; (7) the analytical method used (*cf.* Fisher and Carter, *l.c.*; Shaw, Milling, 1933, **81**, 394 and 396; Strowd, *l.c.*).

Since milling processes vary in different countries, the brans from these countries are not strictly comparable. Some analyses are given in Table 2.

Isaachsen and Ulvesli, 36th Rpt. Inst. Animal Nutrit., Roy. Agric. Coll. Norway, 1933, 675 (Nutrit., Abs., 1933, **3**, Abs. 1418) published analyses referring to Norway, and Bazilevskaya, Jaroslav Zöotechn. Expt. Stat., Work for 1926, 1927, 107 (Amer. Chem. Abs. 1928, **22**, 998) figures for Russian-milled bran.

In articles by Fisher and Carter (*l.c.*), and Fisher and Shaw (J. Min. Agric. 1934, **41**, 255),

TABLE 2.

Country	Reference	Moisture	Ash	Protein	Fat	Crude Fibre	N-free ext.	Starch.	Pentosans.
		%	%	%	%	%	%	%	%
U S.A.	Jacobs and Rask, Ind Eng Chem. 1920, **12**, 899.	13 00	6 45	16 49	3 58			9 07	22 72
	Jacobs and Rask (cited by Kent-Jones, "Modern Cereal Chemistry," p. 219, North Pub. Co, Liverpool, 1927).	8 79	6 38	(N= 2 33)	4 06	10 84			25 07
	Teller, 8th Int Cong Appl Chem. 1912, **13**, 277 (cited by Winton, p 211)	11 80	5 00	14 65 (true)	3 80	11 3		16 3	23 73
	Snyder, U S. Dept Agr Off Exp. Sta 1901, Bull. 101 (cited by Winton, p 212)	9 99	6 06	14 02 (N × 5 7)	4 39		65 54		
England	Kent Jones, p 209.	15 50	5 13	12·89	2 94				
	Woodman, J Min. Agr 1923, **30**, 593.		6 61	16 38	5·30	10 87			
	Smetham and Dodd (Roy. Lanc. Agric. Soc, Milling, 1933, **80**, 232)	11 45	4 25	16 46	4 33	6 50			
France	*Alquier, Ann falsif* 1927, **20**, 445	14 02	6 84	15 162	3 266			13 200	30 00
	Bruère, J Pharm Chim 1931, **14**, 5	12	6	15	5		56		
Germany [2]	Katning and Schleimer, Z Getreidew 1913, **5**, 199ff. (cited by Neumann in "Brot getreide u Brot," p 239, Paul Parey, Berlin, 1929)		5 82 [1] 7 59	18 30 [1] 17 39	5 38 [1] 5 15	9 87 [1] 11 60	60·75 [1] 58 54	15 65 [1] 8·74	22 52 [1] 30 49
Hungary	Weiser, Kiserlét Koz lem, **14**, 581 (Chem. Abs 1912, **6**, 2963).	13 [1] 13	5 98 [1] 6 78	15 3 [1] 15 3	4 5 [1] 3 6	9 45 [1] 8 91	51·77 [1] 52·21		
Canada	Shutt and Hamilton, Canad. Dept. Agr. 1922, Bull. 2, New Ser.			15 0 (min)	3 5 (min)	11·5 (max)			
Australia	Jewell, J. Dept. Agric. Victoria, 1934, **32**, 212 (F.A Q. samples for 1929–34).		3 55–4 67	12 44–15 57					
New Zealand	Foster, N.Z. J. Agric. 1924, **28**, 315.	11 04	5 48	(N= 2·14)		11·41			
	N.Z. J. Agric. 1927, **35**, 19.	12·11	5 00	13 55	3 70	10 68			

[1] Where 2 sets of figures are bracketed together, the first row refers to fine, and the second to coarse bran.
[2] *See also* Mach and Hermann, Landw Versuchs -Stat. 1934, **119**, 11

a review is given of investigations into the fibre content of British wheatfeeds carried out by Wood and Adie, by Woodman and by the Research Assoc. of British Flour-Millers in collaboration with the National Association of British and Irish Millers. It is pointed out that as far as the fibre content is concerned there is no difference between bran and broad bran, and that wheatfeed of a higher fibre content than 7½% should be considered as bran. The highest fibre content found for bran was 10·3%, which was below the average, 10·8%, found by the earlier workers.

It was shown by Fisher and Carter that variations in the composition of the grist and in percentage of screenings included are not dominant factors in the variability of the fibre content of wheatfeed (including bran); the dominant factors are the percentages of bran and flour extracted.

R. Geoffroy (Bull. Soc. Chim. 1932, [iv] **51–52**, 1491) found that wheat bran contains 0·10% glucose+fructose, and 5% sucrose+lævulosides.

Values for the mineral content of wheat bran are given in Table 3.

TABLE 3.

Country.	Reference.	Ash.	Composition of Ash.				
			Fe_2O_3	MgO	K_2O	P_2O_5	CaO
		%	%	%	%	%	%
U.S.A.	Sullivan and Near, Ind. Eng. Chem. 1927, **19**, 499.	6·748	0·200	17·60	26·04	51·57	2·40
	Teller, Arkansas Agr. Exp. Sta. Bull. 42, 70; Winton, p. 240.	5·25	0·277	14·76	28·19	52·81	2·50
Germany	Dempwolf, Ann. Chem. Pharm. 1869, **149**, 343; cited by Neumann, *ibid.* p. 243, and by Nuret, *l.c.*	A5·24	0·21	16·86	30·67	50·15	2·78
		B5·68	0·44	17·35	30·14	49·11	2·50
	Loew, Z. Getreidew. 1914, **6**, 32.	5·50	0·68	16·95	27·88	50·58	2·97
			Fe	Mg	K	P	Ca
Germany	Harding and Dysterheft, Cereal Chem. 1927, **4**, 47.	4·868	0·113	9·254	—	23·30	1·982
U.S.A.	Sullivan and Howe, Cereal Chem. 1929, **6**, 398.	7·177	—	10·08	—	22·76	1·7
			As % of Bran.				
			Fe	Mg	K	P	Ca
U.S.A.	Sherman, " The Chemistry of Food and Nutrition," 4th ed., 1933, p. 559 (Macmillan & Co., New York).		0·0078	0·511	1·217	1·215	0·12

Further data for some of the rarer minerals present in wheat bran will be found in : Bailey, " The Chemistry of Wheat Flour," p. 152 ; Bertrand and Benzon, Bull. Soc. hyg. aliment. 1928, **16**, 457 ; Compt. rend. 1928, **187**, 1087; Compt. rend. Acad. Agric. France, 1928, **14**, 1303 ; Bull. Soc. chim. 1929, **45**, 168 ; Bertrand and Lévy, Bull. Soc. chim. 1931, [iv] **49**, 1417 ; Bertrand and Mokragnatz, Compt. rend. 1922, **175**, 458 ; Bull. Soc. chim. 1930, [iv], **47**, 326; Bertrand and Rosenblatt, Compt. rend. 1921, **173**, 133; Bertrand and Silberstein, Ann. Agron. Nov.–Dec. 1933 (Int. Rev. Agric. 1934, **25**, 175T); Birckner, J. Biol. Chem. 1919, **28**, 191; Bruère, Compt. rend. 1934, **198**, 504; Davidson, Cereal Chem. 1929, **6**, 132; Dempwolf, Ann. Chem. Pharm. 1869, **149**, 343; Elvehjem and Hart, J. Biol. Chem. 1929, **82**, 473; Jadin and Astruc, Compt. rend. 1914, **159**, 268; Javillier, Bull. Soc. chim. biol. 1930, **12**, 709; Lindow, Elvehjem and Peterson, J. Biol. Chem. 1929, **82**, 465; Lindow and Peterson, *ibid.* 1927, **75**, 169; Loew, Z. Getreidew. 1914, **6**, 32; McClendon and Hathaway, J. Amer. Med. Assoc. 1924, **82**, 1668; McHargue, J. Agric. Res. 1925, **30**, 193; J. Amer. Soc. Agron. 1925, **17**, 368; Sherman, " The Chemistry of Food and Nutrition " (New York: MacMillan & Co., 4th ed., 1933), p. 559; Sullivan and Howe, Cereal Chem. 1929, **6**, 398; Sullivan and Near, Ind. Eng. Chem. 1927, **19**, 499; Teller, Arkansas Agr. Exp. Sta. Bull. 42, 70; Winton, p. 243.

Table 4 gives analyses of rye, maize, oat, and rice brans.

TABLE 4.—ANALYSES OF RYE, MAIZE, OAT AND RICE BRANS.

Cereal	Reference	Moisture.	Ash.	Protein.	Fat.	Fibre.	N-free ext.	Starch.	Pentosans
		%	%	%	%	%	%	%	%
Rye	Winton (p. 260). U.S. 1878–1881	11·59	1·86	10 58	1·66	1·67	72 64		
	1886	13·37	1·76	12 03	1·84	1·36	69 64		
	1909	9 38	2·18	13 44	1·83	2 30	80 24		
	Winton (p 260). Germany	13 37	2 09	11·17	1·63	2 62	69·12		
	Neumann (p 238)		4 83	17·58	3 62	—	—	20 49	22 59
Maize	Winton (p 80): white	10·13	2·16	8 43	6 71	9·72	62 85		
	yellow	10 37	2·70	9 06	11·00	9 68	57·19		
	Consolani (Il Coltiva tore, 66, No. 1, 10, Chem Abs. 1921, 15, 3154)	13 20	5 80	14·10	3·70		56 00		
Oats	Miner (Winton, p. 168)	6 50	2 60	19 30	7 10	4 60	59 90		
Rice	Wise and Broomell, (U S. Dept. Agric. 1916, Bull. 330; Winton, p. 138): Honduras	9 61	10 58	13 41	10 65	11·70			9 95
	Japan	9 39	11·33	12 81	15·13	12 54			11·40
	Joachim and Kandiah (Trop. Agriculturist, Ceylon, 1928, 70, 195; Chem. Abs. 1929, 23, 1962 T): Ceylon	12·51	11·44	13·17	10·12	14 05			
Millet	Bersch, Landw. Versuchs Stat. 1895, 46, 103	10·27	8·72	6 68	2 33	52 50	19 50		
	(Winton, p. 124)	9 65	9·36	6·25	2·38	43 78	28·58		
Buckwheat (*hulls*)	Coe, U.S. Dept. Agric Circ. 190 (1931)	9·77	2·15	4·11	0 86	45 97	37·14		

Data as to the composition of the various by-products of rice milling are to be found in Winton (p. 136ff); the U.S. Dept. Agric. Bull. 570 (1917); Strowd's "Commercial Feeds," Bull. Imp. Inst. 1918, 16, 16; Hand *et al.*, Missouri Agric. Exp. Sta. Res. Bull. 123; Stieltjes, Bull. Mat. Grasses Inst. Colon, Marseilles, 1922, 201; Bertrand and Benzon, Compt. rend., Acad. Agric. France, 1928, 14, 1303; Bull. Soc. hyg. aliment. 1928, 16, 457; Fraps (Winton, p. 152); Joachim and Kandiah, *l c.*

Belland (Ann. Falsif. 1918, 11, 388) supplies data for the bran of Morocco beans, and an article on "Composition of commercial mustard bran with special reference to the detection of added mustard bran in prepared mustard" is to be found in J. Assoc. Off. Agric. Chem. 1923, 7, 170 (Hertwig and Palmore). Analyses of other less commonly used cereals, nuts, and oil seeds are given in Winton.

The following is a list of references dealing with the detection of adulteration in wheat bran: Amos, Analyst, 1929, 54, 332; Collin, Ann. Falsif. 1917, 10, 539; Estienne, J. Pharm. Belg. 1933, 5, 89 and 105 (Muhlenlab. 1933, 3, 80); Agricultura, 1933, 36, 91 (Amer. Chem. Abs 1933, 27, 5430); Evans and Wallis, Analyst, 1928, 53, 432; Fonzes-Diacon, Ann. Falsif. 1924, 17, 528; Lopriore, Staz. sper. agr. ital. 1916, 48, 297; Marchadier and Goujon, Ann Falsif. 1924, 17, 328; *ibid.* 1924, 17, 458; Raunier and Pau, Ann. Falsif. 1930, 23, 229 The adulteration of rice bran is dealt with by Silverberg (J. Assoc. Off. Agric. Chem. 1921, 5, 77; 1922, 6, 71). (*See also* the list of articles on "Corn Cockle" to be found in

the discussion of the nutritive value of bran, below.)

Durham (Cereal Chem. 1925, **2**, 299) found that the water absorption of bran diminished (from 29 to 17%) according to the extent to which the bran had been ground.

Täufel and Thaler (Z. Unters. Lebensm. 1934, **68**, 631) have compared the pentosan content of crude fibre prepared from bran (rye and wheat) by the Weender process (2·3–3·0% pentosans in wheat bran, 1·6–2·8% in rye bran) and by König's method (no pentosans). Tollens *et al.* found 22–25% of pentosans in wheat bran, and 40% in maize bran. Norris and Preece (Biochem. J. 1930, **24**, 59) isolated four chemically and physically distinct fractions from the hemicelluloses of wheat bran, two of them containing small percentages of uronic acid residues. Hemicellulose B2 was apparently a glucosan, while the other fractions consist largely of pentose residues. Thomas and Kapfhammer (Pflüger's Archiv. 1923, **201**, 6) by means of utilisation experiments found that 27·3–29·4% of the cell membranes of bran consisted of cellulose and hexosan. Investigations on the pentosan and cellulose content of cereal hulls were also carried out by Rubner (Amer. Chem. Abs. 1917, **11**, 2512) and by Porst (8th Int. Congr. Appl. Chem. 1912, **13**, 205; Winton, p. 88).

Comparatively little work has been carried out on the proteins of wheat bran. Snyder (Minnesota Agric. Exp. Sta. 1899, Bull. 63, p. 527) supplies data for the *nitrogen content* of various fractions of the protein of wheat bran, and Teller (Arkansas Agric. Exp. Sta. Bull. 42) found distinctly less gliadin and relatively more albumin and globulin in commercial bran than in the flour from the same wheat.

Hamilton *et al.* (J. Amer. Chem. Soc. 1923, **45**, 815) obtained the following values for the distribution of nitrogen (as percentage of total nitrogen in the feed) in wheat bran proteins: total basic N 24·02; ammonia N 9·17; humin N 6·86; arginine N 11·99; cystine N 0·81; histidine *N* 7·32; lysine *N* 3·90; mono-amino acid N, amino N in filtrate from bases 38·07; proline, oxyproline, tryptophane, etc., non-amino N in filtrate from bases 3·59; ether-soluble N 0·04; alcohol-soluble N 1·23; non-protein N soluble in cold, 1%, CCl_3CO_2H in filtrate from colloidal iron 15·26% (*cf.* the results obtained by Nollau, J. Biol. Chem. 1915, **21**, 611; Winton, p. 227).

Jones and his collaborators (J. Biol. Chem. 1923, **58**, 117; 1924, **62**, 183; 1925, **64**, 241) carried out a series of investigations on the proteins of wheat bran. Their results are summarised in Table 5.

TABLE 5.

Protein.	% of total protein in bran.	Nitrogen Distribution in Bran Proteins.						
		% Free NH_2—N	% Cystine.	% Arginine.	% Histidine.	% Lysine.	% Tryptophane.	% Tyrosine.
Albumin . . .	16·64	2·84	3·29	10·04	2·57	4·51	4·76	4·20
Globulin . . .	13·62	6·59	1·52	14·13	2·76	11·84	2·85	3·69
Prolamine . .	31·01	1·88	2·29	4·41	0·84	2·45	1·37	3·38

The tryptophane content of the albumin of wheat bran was the highest of any plant protein until then reported; the proteins are also high in cystine.

G. L. and W. K. Teller (Cereal Chem. 1932, **9**, 560; *see also ibid.* 1932, **9**, 261) studied the content and composition of the non-protein constituents of wheat bran; not more than 25% are in the form of amides of the type of asparagine. The results indicated that 5·7 should be used as the factor for converting N into crude protein content in the case of wheat and its bran.

Nottbohm and Mayer (Z. Unters. Lebensm. 1935, **69**, 289) found that the magnesia extract of wheat bran mainly consists of betaine, which is found in small quantities in the phosphatides of wheat and oats.

Table 6 summarises some of the physical constants obtained for the oils from various cereal brans.

TABLE 6.

Cereal.	Reference.	Sapon. No.	Iodine No.	Unsaponifiable.	Free Acids.	Neutral Fat.	Total Acids.	Mol. Wt. of Fatty Acids.
				%	%	%	%	
Wheat	Stellwaag, Landw. Versuchs-Stat. 1890, **37**, 135 (Ball, Cereal Chem. 1926, **3**, 21).	183·1	—	7·45	14·35	78·73	89·71	285·0
Rye	Ball, *ibid.* 1926, **3**, 24.	175·1	—	7·64	16·44	78·31	93·75	285·6
Millet	Bersch, *ibid.* 1895, **46**, 103; Winton, p. 125.	213–216	58–59					
Rice	De 'Conno and Finelli, Ann. Chim. Appl. 1930, **20**, 26; Winton, p. 147.	189·1	100·77	1·415				

Both rice bran and the oil obtained from it rapidly increase in acidity unless specially treated. Brown (Winton, p. 146) has shown that this deterioration is due to the activity of lipase. Heating at 93°C. destroyed the enzyme and hence reduced the amount of free acids formed The m p of rice oil is 24°–25°. Results obtained by De 'Conno and Finelli (*l.c.*) indicated that the original fat consisted of glycerides of oleic, linoleic, arachidic, stearic, and palmitic acids Weinhagen (Z physiol Chem. 1917, **100**, 159; Winton, p. 148) states that rice bran contains 10 94% of fat, 73% of which is liquid and 27% solid. The liquid portion consists of 91% fatty (59% oleic and 31 8% palmitic) acids and 5 3% of phytosterols, the solid fat consists of 90 6% fatty acids, almost entirely consisting of palmitic acid, and 4·7% of phyto sterols

The phytosterols in wheat bran have been discussed by Ellis (Biochem. J. 1918, **12**, 160), Leulier and Crevat (J. Pharm Chim. 1931, **14**, 214) and by Anderson and his associates (J. Amer. Chem. Soc. 1924, **46**, 1717). The last mentioned workers isolated dihydrositosterol (m.p. 144°–145°) from the unsaponifiable fraction of the petroleum-ether extract of wheat bran; sitosterol was also present.

Andrews and Bailey (Ind. Eng. Chem. 1932, **24**, 80; *see also* Leulier and Crevat, *l.c.*) supply the following data for the distribution of organic phosphorus in wheat bran.

	Total.	Phytin.	Lipoid.	Inorg and nucleic.	Extracted by 2% HCl.
	%	%	%	%	%
Found . . .	1 646	1·415	0 028	0 203	1·61
Percentage of total P	—	85 96	1·7	12 33	97 8

Sullivan and Near (Cereal Chem 1928, **5**, 163, 436) investigated the lipoid phosphorus of wheat and its milling products

Anderson, after a series of studies (J Biol. Chem 1912, **12**, 447, 1914, **18**, 425, 441; 1915, **20**, 463), concluded that phytic acid or phytin, a substance first isolated by Posternak (Compt rend. 1903, **137**, 439) is inositol hexaphosphoric acid, $C_6H_{18}O_{24}P_6$ or $C_6H_6(OH_2PO_3)_6$. [According to Patten and Hart (New York Agric Exp Sta Bull 250, 1904) 80 5% of the water-soluble phosphorus of wheat bran exists as a Mg–Ca–K salt of a phospho organic acid which may be split up into phytin] Averill and King (J. Amer Chem Soc. 1926, **48**, 724) found 4 53% of phytin (calculated as $C_6H_{18}O_{24}P_6$) in wheat bran. After a series of investigations (J. Amer Chem. Soc. 1913, **35**, 890; *Ark Agric Exp Sta Bull 138*, *J. Amer* Chem Soc. 1918, **40**, 523) J. B. Rather adopted the formula $C_6H_6(OH)(OH_2PO_3)_5$ or $C_6H_{17}O_{21}P_5$ for an inosite phosphoric acid which he isolated from wheat and rice bran.

The following is a list of other investigations relating to the phosphoric compounds of wheat bran: Robinson and Mueller, Biochem. Bull. 1915, **4**, 100; Arbenz, Mitt. Lebensm. Hyg. 1922, **13**, 45; Rogozinski, Bull. Acad. Sci. Cracovie (B), 1915, No 5, 87; Amer. Chem. Abs. 1922, **16**, 3499. According to the last mentioned author, bran forms one of the three chief sources of phytic acid.

In comparison with wheat bran, rye bran is comparatively poor in phytin P_2O_5, but is rich in inorganic P_2O_5 (Rogozinski, *l c.*). Calò (Annali Chim. Appl. 1935, **25**, 49), in an article on the phospho organic compounds in products obtained on grinding germinated barley, found that the proportion of inositol hexaphosphoric acid was at a maximum in bran.

Phytosterol was obtained in a crystalline state from rice bran by Tsujimoto (Winton, p. 148; *see also* Nabenhauer and Anderson, J. Amer. Chem. Soc. 1926, **48**, 2972). Suzuki *et al.* (Bull. Col. Agric. Tokyo, 1907, **7**, 503; *see also* Bernardini, Atti. R. Accad. Lincei, 1911, **21**, 283; Borasio, Giorn Risicolt. 1929, **19**, 131) found that rice bran contained 8% of phytin; and Thompson found 2 291% of phosphorus and 8 22% of phytin (J Agric. Res. 1915, **3**, 425).

Suzuki *et al.* (J. Coll. Agric. Tokyo, 1909, **1**, 77, Winton, p. 142) found in rice bran 1·16% of nitrogen (prolamines) soluble in 60% alcohol and 1 37% of N (globulin) soluble in 10% salt solution; 0 2% caustic soda solution dissolved 1·51% of the bran, consisting of leucine 8 6, glutamic acid 4 7, tyrosine 0 3, arginine 3 4, histidine 0 88, and ammonia N 1·13%.

Oryzanin, a crude material isolated from rice bran by Suzuki *et al.* (Biochem. Z. 1912, **43**, 89; Winton, p. 144), contains a substance to which rice owes its antiscorbutic properties. A general résumé of the proteins of rice bran is given by West and Cruz (Philippine J. Sci. 1933, **52**, 1).

A number of Japanese workers (Mem. Coll. Sci. Kyoto, Ser. A, 1928, **11**, 481, 497, 505, 517, 521) have investigated the composition of *pityrol*, obtained by the distillation of rice bran. Uzawa (J. Biochem. Japan, 1932, **15**, 1 and 11) describes the preparation of the phosphoesterases of bran.

Giesen (Inaug. Dis. Bern, 1909; Winton, pp. 237 and 267) found 1·1% of protease (optimum temperature 30°–40°C.) in wheat bran, and 0 9% in rye bran (optimum temperature 30°–45°), calculated as trypsin. According to Kuhl (Mühle, 1934, **71**, 1413 and 1445), the dark colour developing in bran particles of flours on making up into doughs is due to the presence of oxydases

Schulerud (Muhlenlab. 1933, **3**, 137) stated that the yellow colour which develops on extracting rye and wheat milling products with a mixture of 50% of acetic ester, 30% of alcohol,

and 20% of water, and adding potassium carbonate, is due to a pigment located in bran which acts as an indicator (colour change at p_H 7·0–9·0). Microscopic investigation shows that this pigment is not a starch degradation product, but it may be identical with the flavone discovered by Anderson (Canad. J. Res. 1932, **7**, 285).

The following is a list of articles dealing with the nutritive value of wheat bran from a general point of view: Alquier, Ann. Falsif. 1927, **20**, 445; Bazilevskaya, *l.c.*; Fraps, Texas Agric. Exp. Sta. 1922, Bull. 291; Neal, Nat. Amer. Miller, 1934, **62** (8), 52; Randoin, Alquier *et al.*, Compt. rend. 1924, **179**, 1342; Woodman, J. Min. Agric. 1923, **30**, 593; Lindsey, Mass. Agric. Exp. Sta. Bull. Rpt. 1908, 158; Rothwell, Canada Exp. Farms, Anim. Husb. Div. Rpt. 1924, 11.

Hansson (Meddl. Centralanst. Försöksv. Jordbrukssområdet, Sweden, 1924, No. 273; Exp. Sta. Rec. 1925, **53**, 666; *cf.* Brückner and Dietz, *l.c.*) found wheat bran to be a more valuable feed for milk cows and work horses than for swine; it was somewhat less valuable for milk production than ground oats, but could make up 30–40% of the ration without serious consequences. Rye bran was similar in effect to wheat bran. In large amounts it caused a marked reduction in milk production with an increase in fat content (*see also* Stockklausner and Daum, Züchtungsk. 1931, **6**, 341 (Nutrit. Abs. 1932, **1**, Abs. 1964) and Ampi, Mühle, 1933, **70**, 270). Both wheat and rye bran had undesirable influences on the quality of lard in pigs. Barley bran was better for pigs, though it decreased the dressing percentage, it improved the quality of the lard. Oat bran is a very bulky and relatively poor feed; it is best utilised by horses and cattle. The fodder value of rye brans of different milling grades was investigated by Honcamp and Pfaff (Landw. Versuchs.-Stat. 1925, **103**, 259). Maize hulls are separated and mixed with maize gluten and soluble products to give gluten feed, used for dairy cows, stock, chickens, etc. (Phillips and Boerner, U.S. Dept. Agric., Bur. Agric. Econ. 1925). Fraps (Texas Agric. Exp. Sta. 1922, Bull. 291) supplies tables showing the results of feeding tests with maize, bran, etc.

Bran is largely used as a food for farm animals but has a weakening effect upon the digestion if used in large quantities. It is more suitable as a food for fattening than for working animals. If used largely for milk cows, it tends to make the butter soft. Similarly, large quantities of bran given to fattening animals tend to lower the melting-point of the body-fat (*cf.*, however, Callow, Empire J. Exp. Agric. **3** (9); Food, 1935, **4**, 267). This is an advantage in the production of mutton or beef, but a disadvantage with bacon.

Crichton and Allcroft (Scot. J. Agric. 1932, **15**, 63) in experiments with crossbred Aberdeen Angus cattle found that fattening animals made greater gains at a slightly lower cost per lb. on bran than on linseed cake meal.

Schmidt and Zöllner (Bied. Zentr. Agrik. Chem., Abt. B. Tierernähr. 1931, **3**, 23) found that wheat bran exerted an unfavourable effect on the laying capacity and general health of poultry. Shaw and Fisher (*l.c.*) criticise Halnan's results (Min. Agric. Fish. Bull. 7, 2nd ed., 1932) in regard to the unfavourable effect of the bulkiness of bran on poultry, and point out that it is the bulkiness of *wet*, not dry, bran which must be considered. Tulley (S. Dakota Sta. Rpt. 1932) determined the feeding value of wheat by-products for poultry.

The following is a list of articles dealing with the detection of corn cockle in bran and its effect on stock: Becker (Zentr. Bakt., Abt. II, 1918, **48**, 417); Brandl (Landw. Versuchs.-Stat. **72**, 326); Broquet (Bull. Assoc. Chim. Sucr. 1932, **49**, 27); Grünewold (Mühle, 1933, **70** 105); Quigley and Waite (Maryl. Sta. 1931, Bull. 325, 343); Rogozinski and Glowczynski, Polish Acad. Sci. Letters, 3rd July, 1933; Bull. Acad. Polonaise, 1933, *B*, 189–203; Schneider, Arch. Geflügelk. 1933, **7**, 121 (Nutrit. Abs. 1933, **3**, Abs. 2630); Strowd's "Commercial Feeds" (p. 121); I. Weiser, Kiserlet Közlem. 1924, **27**, (1–2), 1 (Exp. Sta. Rec. 1926, **54**, 160; Fortschr. Landw. 1927, **2**, 6).

The digestibility of bran by man and by animals has been the subject of a considerable number of investigations [*see, e.g.*, Moeller, Z. Biol. 1897, **35**, 291; Rubner, *ibid.* 1883, **19**, 45; Holmes, U.S. Dept. Agric. 1919, Bull. 751; Honcamp and Nolte, Landw. Versuchs.-Stat. 1920, **96**, 121; Hindhede, Mediz. Welt, 3, 158 and 192 (Z. Unters. Lebensm. 1933, **65**, 242); Emmerich and Loew, Z. ges. Getreidew. 1913, **5**, 115; Lindner, *ibid.* 1929, **16**, 951; Mohs, *ibid.* 1929, **16**, 45; Monceaux, Compt. rend. Soc. biol. 1923, **89**, 402; D.Sc. Thesis, Paris, 1924 (Amer. Chem. Abs. 1925, **19**, 1741)]. Cellulose is, at best, but imperfectly digested by man, and that which has become lignified, hardly at all. Formerly it was held that the contents of the aleurone cells could not be digested by man, but Heupke (Z. Ernährung, 1932, **5**, 138) claims to have demonstrated experimentally that enzymes are able to diffuse through the walls of the aleurone cells and digest their contents without attacking the cell walls. These investigations do not, however, if substantiated, affect the unfavourable nitrogen balance which has been established for wholemeal bread.

Brunnich and Rawson (Queensland Agric. J. 1921, **15** (5), 195 and (6), 235) determined the digestion coefficients for Australian wheat bran on four wethers, and suggested that the higher digestibility of the crude fibre of Australian, as compared with U.S. and German, bran is due to the more rapid growth of plants in Australia. Tests for the digestibility of wheat bran for sheep were also carried out by Saito (Imp. Zöotech. Exp. Sta. 1931, Bull. 26; Amer. Chem. Abs. 1932, **26**, 1323) and by Suzuki (Imp. Zöotech. Exp. Sta. 1931, Bull. 27; Amer. Chem. Abs. 1932, **26**, 1323). Chaussin (Compt. rend. Soc. biol. 1919, **82**, 269) studied the digestion of bran by the rabbit and dog.

Examples of processes for rendering bran more digestible are those due to Monti (Atti 1° Congr. int. Panificazione, Roma, 1932, 228 (1933)), and to Rabinovitch (B.P. 392054).

Falcon-Lesses (J. Nutrit. 1930, **2**, 295) and Cowgill and Anderson (J. Amer. Med. Assoc. 1932, **98**, 1866; and 1933, **100**, 795) found

that the laxative effect of bran was not due to its phytin content but to the amount of fibre and pentosans present; similar conclusions were arrived at by Rose *et al.* (J. Amer. Dietet. Assoc. 1932, 8, 133). Olmsted *et al.* (Proc. Soc. Exp. Biol. Med. 1934, 32, (1), 141) conclude that the pentosans of bran do not exert a laxative effect, while bran fibre is definitely laxative.

Murphy and Jones (J Biol. Chem. 1926, 69, 85) state that, taken collectively, the wheat bran proteins contain over twice as much of the so-called nutritionally essential amino-acids (tryptophane, tyrosine, cystine, lysine, and arginine) as the same amount of wheat endosperm (*see also* Hamilton *et al.*, J. Amer. Chem. Soc. 1923, 45, 815).

Klein *et al.* (Amer. J. Physiol. 1926, 76 (2), 237) describe investigations into the nutritive value of the various layers of the wheat and maize kernels.

There was a widespread belief that bran is particularly well fitted, because of its richness in minerals, to supply the needs of animals with reference to the development and nutrition of bone. Experiments carried out in South Africa (Ingle, J. Comp. Path. & Therapeutics, March, 1907, and J. Agric Sci. 1908, 3, 22) and by Bang (Kong. Vet.-Landsbehejskole Aarskrift, 1925, 383) on horses have proved that there is a definite deficit of lime in the lime-phosphorus ratio of bran from this standpoint. Carles (Rep. pharm. 25, 97) discusses the value of the phosphates of wheat bran in animal feeding.

Bunge (Z physiol. Chem. 1898, 25, 36, quoted by Sherman, "Chemistry of Food and Nutrition," p. 328, Macmillan, N.Y., 1933) demonstrated that rats fed on bread made from flour containing bran made greater general growth and developed a greater amount and higher percentage of hæmoglobin than rats fed on flour without bran. Rose and Vahlteich (J Biol. Chem. 1932, 96, 593) state that whole wheat appears to contain certain factors, lacking in patent flour, which supplement the effect of inorganic iron and copper added to the diet in regenerating hæmoglobin.

Sherman (p. 568) states that wheat bran contains (+) vitamin A, and G(B_2), and may be a *good source* (++?) *of vitamin* $B(B_1)$. (*See also* Cramer and Mottram, Lancet, 1927, II, 1090; Halliday, J. Biol. Chem. 1934, 106, 29; Halliday and Dennett, J. Nutrit. 1934, 7, Proc. 12; Kramer and McCammon, Kans. Agric. Exp. Sta., 6th Biennial Rep. 1932, 113; Marchlewski and Wierzchowski, Pam. Panst. Inst. Nauk. Gosp Wiejsk. Pulawach, 1922, 2, *A*, No. 1, 160; No. 2, 161 (Amer. Chem. Abs. 1924, 18, 1319); Plimmer *et al.*, Biochem. J. 1931, 25, 691; Rose *et al*, J. Amer. Dietet. Assoc. 1932, 7, 369; Stammers, Biochem. J 1921, 15, 489.)

Mitchell and Villegas (*J. Dairy Sci.* 1923, 6, 222) found that the nutritive value of rice bran proteins was approximately the same as that of soya beans; very little supplementary effect was noted between the proteins of rice bran, soya beans and cotton seed meal. The nutritive value of rice proteins was also investigated by West and Cruz (*l.c.*). Davies (Fertilisers, Feeding Stuffs, and Farm Supplies J. 1927, 12, 315) supplies data for the composition and feeding value of rice bran and various oat and barley by-products.

The content of the so-called vitamin-B complex in rice bran has been the subject of a number of articles, of which the following is a list: Annl. Rep. Bur. Sci. Philippine Isl. 1931; Kinugasa, J. Pharm. Soc. Japan, 1928, 48 (6), 539; Kinugasa and Hattori, *ibid.* 1922, No. 485, 579, No. 486, 671, No. 487, 780; *ibid.* 1924, No. 508, 469; Otake, J. Agric. Chem. Soc. Japan, 1931, 7, 775; Stechow and Wamoscher, Arch. Pharm. Inst. Univ. Berlin, 1927, 13, 145; Titus, Poultry Sci. 1932, 11, 117; Titus and Ginn, Science, 1931, 74, 249; Ikeda, J Orient. Med. 1924, 2, 90; Tsukiye, Biochem. Z. 1922, 31, 124; Van Veen, Mededeel. Dienst Volksgezondheid. Nederland. Ind. 1931, 20 (2), 73, 80, 97; 1932, 21, 184; Rec. Trav. chim. 1932, 51, 265 and 279; Z. physiol. Chem. 1932, 208, 125; Windaus *et al.*, Nachr. Ges Wiss. Göttingen, Math-physik. Klasse, 1932, 342.

Apart from its use as a feeding stuff and, when solubilised and disintegrated (*see, e.g.*, Monti's and Rabinovitch's processes mentioned above), in brown and other loaves, bran has been proposed for use in cereal foods and beverages, as a baking improver, for the manufacture of furfuraldehyde (Utaka, Rep Osaka Ind. Res. Lab. Japan, 1925, 5, 1; Amer. Chem. Abs. 1925, 19, 2336), xylose (Pacini, Nat Amer Miller, 1934, 62 (9), 30; Emley, Ind. Eng Chem., News Ed, 1928, 6 (21) 3), active charcoal (Northwestern Miller, 1933, 174, 588, June 14), fuels or building materials (Mühle, 1932, 69, 1068), and rayon or celluloid (Gross, B.P. 361588; J. Text. Inst. 1932, 23, A166). Bran is also used, although to a diminishing degree, in tanning leather (for a description of the process and of the changes occurring in the fermentation of bran so employed, *see* Wood and Wilcox, J.S.C.I. 1893, 12, 422, and 1897, 16, 510), and as a cleaning material (*e.g.* for furs). E. A. F.

BRANDY. The term *brandy* is an abbreviation of *brandywine*, the original English form of the German *Branntwein* or the French *Brandevin*. The European variations of the term, however, have wider applications than that in Britain Thus in Germany it is applied to any spirituous liquor obtained by distillation, whilst in France the alternative title *Eau de Vie* legally includes spirit distilled from cider, perry, cherries, plums, and *marc* as well as that obtained from wine. Since 1880 the British term *brandy* has been restricted to spirits obtained by distillation from fermented grape juice. An Act passed by Parliament in 1690 states in the preamble, "Whereas good and wholesome brandies, aqua vitae and spirits may be drawn and made from malted corn, etc.," but the Spirits Act of 1860 prescribed that "all spirits which shall have had any flavour communicated thereto and all liquors whatsoever which shall be mixed or mingled with any such spirits shall be deemed a British compound called *British Brandy.*" This section was repealed in 1880 Under the title *Spiritus Vini Gallici* the British Pharmaceutical Codex (1934) states that

"brandy is obtained by distillation from the wine of grapes, and matured by age. It occurs as a pale amber-coloured liquid having a characteristic odour and taste and, as a rule, a slightly acid reaction. It contains about 40% v/v of ethyl alcohol and usually about 0·05 to 0·15% of higher alcohols, 0·1 to 0·15% of esters, 0·05 to 0·2% of volatile acid, 0·0005 to 0·002% of furfural, and 0·02 to 0·04% of other aldehydes." According to the United States Pharmacopœia of 1936 "*Spiritus Vini Vitis* is an alcoholic liquid obtained by the distillation of the fermented juice of sound, ripe grapes and containing at 15·56°C. not less than 48% and not more than 54% by volume of ethyl alcohol. It must have been stored in wood containers for a period of not less than four years." It is "a pale amber-coloured liquid, having a characteristic odour and taste and an acid reaction: specific gravity from 0·933 to 0·921 at 25°C."

Consumption.—In common with that of all other spirituous liquors, the consumption of brandy has decreased during the past decade, as will be seen by the following statement of the number of proof gallons retained for home consumption in Great Britain and Ireland, although the official return for 1936 indicates a partial recovery.

Year.	Proof Gallons.
1925	633,747
1926	591,345
1927	570,428
1928	542,464
1929	539,918
1930	487,137
1931	461,498
1932	396,291
1933	411,475
1934	401,645
1935	395,308
1936	422,213

Production.—Approximately 95% of the brandy imported into the United Kingdom comes from France, the finest grades being Cognac and Armagnac, so named from the French towns in which originally they were distilled. Whilst the term *Cognac* has by custom come to be used almost as a generic term for *brandy*, it is strictly applicable only to spirits distilled from the produce of grapes grown in the Cognac region, which comprises a certain part of the two departments of Charente and Charente Inferieure, also Dordogne and Les Deux-Sèvres. A strict delimitation of the Cognac area has been made by the French Government by decree dated 1st May, 1909, and the region is locally divided into the Grande or Fine Champagne, the Petit Champagne, the Borderies, and the Bois, according to the quality of the wine produced. Very little brandy is now distilled in Cognac itself, the greater part being produced on the brandy farms of the surrounding districts. The French Government has prohibited the description *Cognac* to be applied to any mixture of Cognac or other wine spirit with grain or beet spirit and has further provided that labels, marks, etc., bearing the word *Cognac* should signify that the spirit in question is solely the product of the Cognac region. Other brandies of less commercial value are those of the Midi and the districts of Aude Gard, Hérault, and Pyrénées Occidentales, commonly known as the *Trois six de Montpellier.* Marc brandies are distilled from the fermented *marc* or refuse of the wine press as well as from the lees of the wine casks. The soil of the brandy-producing districts is mainly calcareous and the grape is a small white berry with very acid juice producing a wine of inferior quality for drinking purposes.

Brandies are produced in most other wine-growing countries, especially when, owing to over-production of wine, or some defect in its quality, it becomes more profitable to convert it into spirit than to dispose of it as wine. Algerian brandy is of high quality, resembling Cognac, and is generally sent to France for re-shipment to England and other countries. The Spanish product is also similar to the French and commands a high price. In Australia and South Africa production is steadily increasing, although the export trade is at present very small. The so-called *dop brandy* of South Africa is produced in the same way as the French *marc brandy* and has similar characteristics. There is considerable production of brandy in Egypt, but it is nearly all distilled from wine made from grapes imported chiefly from Southern Turkey, Greece, Cyprus and Asia Minor. It has a strong characteristic flavour much appreciated by consumers of the cheaper brandies. Spurious brandies of doubtful origin, but described as "Egyptian," have also been placed on the market. They are probably made from the currant grape grown in Greece and Asia Minor and have no right to the title "Egyptian" beyond the fact that they are exported *via* Alexandria.

Manufacture.—The reputation of the brandies of the Cognac and Armagnac districts depending so much upon their bouquet, it is desirable to avoid high rectification and consequent removal of those secondary ingredients upon which the flavour mainly depends. Distillation is usually conducted, therefore, in a simple *pot* still by the professional distiller as well as by the farmer. The still, which varies in content from 150 to 200 gallons, is usually enclosed in brickwork, with only a small bulbous head exposed, and is generally heated by means of a furnace, wood being considered the best fuel. In a few distilleries the stills are heated by steam. Occasionally a subsidiary vessel filled with wine and called a "chauffe-vin" is attached to the still and through it the pipe conveying the spirit vapour to the refrigerator passes, heating the wine so that the latter is quickly raised to boiling-point when subsequently passed into the still, thereby effecting a saving of fuel. Two distillations are made, termed "brouillis" and "bonne chauffe," corresponding respectively with the "low wines" and "spirits" of the whiskey distiller. In some distilleries the finished spirit is produced at one continuous distillation by means of a still

described as "à premier jet." In this form of still a vessel is attached to and above the head of the still, and through it the spirit of the first distillation is conveyed. This spirit is again vaporised by the heat of the spirit vapour rising from the still itself on its way to the refrigerator. The spirit produced in this way is not considered so fine as that obtained by the pot still, but it is of higher strength and more suitable for the manufacture of liqueurs. The quality of the spirit depends greatly on the care with which the distillation process itself is carried out. The stills should be worked slowly and regularly, the normal time for the complete distillation of a charge being about ten hours.

The quantity of wine used in the process of manufacture is relatively very great, the amount of brandy produced from a given measure being only from 10–15%. The strength of the wine varies from 4·5 to 9% by weight of pure alcohol or approximately from 10 to 20% of proof spirit, the average being about 6·5% of alcohol or 14% of proof spirit. The finished spirit as run from the still contains about 64% by weight of alcohol equivalent to a strength of about 25° over proof. The brandy, as received from the farmers, is blended and diluted in vats, sweetened with cane sugar, slightly coloured with caramel, and filtered into storage vats in which it is matured. The simple pot stills and the modified stills known as "à premier jet" as used in the Charente district are not suitable for wines having a strong earthy flavour ("terroir") or other undesirable qualities. In such cases, as the brandies of the Midi, the Rochelle district, and the marc brandies of Burgundy, stills of a more complicated nature are employed owing to the necessity for a greater degree of rectification. In these the distillation is continuous, and in the Rochelle district and in the islands of the north west coast, a pot still with a rectifying head, known as the "Alembic des Iles" is employed, whilst in the south the distilling column consists of a series of compartments separated by plates connected with taps, by means of which it is possible to draw off the spirit at a higher or lower strength as desired. These stills are generally heated by direct fire.

Large quantities of wine are produced in the Midi for conversion into brandy, the grapes of this region being unsuitable for making good wine. This is attributed to the effects of the *Phylloxera* which devastated the whole of the Charente district in the years 1875–1878. Before this time most of the brandy exported to the United Kingdom was genuine Cognac, but the destruction of the Charente vineyards stimulated the production of brandy in other parts of France as well as in other countries. The vineyards of the Cognac district were replanted with American stocks, on which Charente vines were grafted, and the result has been highly successful. In the south of France, however, the vineyards ravaged by the *Phylloxera* were replanted with vines which were not appropriate to the soil, and which yielded wine in great quantity but at the sacrifice of good quality. Hence the use of the rectifying stills in the Midi and the large quantity of brandy produced. Most of this is consumed in France. The spirit derived from diseased or unsound wines is highly rectified and used for industrial purposes. The cheapness of wine, therefore, affords little or no inducement to the distillers of the Midi to use beet or grain as the raw material for the production of their brandies.

Marc brandies or *eau-de-vie de marc* are, as the name implies, derived from the marc or refuse of the grapes after the juice has been extracted. They have a strong earthy flavour and usually are rich in secondary products. They are, therefore, often added to other wine spirits to impart the brandy character, or admixed with neutral spirit from grain or beet in the preparation of factitious brandies.

Composition.—In addition to alcohol and water the principal constituents of brandy include acetic, butyric, and other esters, acetic acid, and a small quantity of volatile oil. When freshly distilled, brandy is colourless. On storage in oak casks it acquires a yellowish brown colour, but in order to give it a fictitious appearance of age, or to standardise the colour to a particular brand, a solution of caramel or burnt sugar is often added. For the same purpose an extract of oak, of the type used for making brandy casks, is also sometimes added. Owing to long usage and the fact that the average consumer would not accept a colourless brandy, this artificial addition of colour may be regarded as a legitimate commercial process.

A comprehensive investigation of the nature of the secondary ingredients of 25-year old brandy was carried out by Ordonneau (Compt. rend 1886, 102, 217) with the following results:

	Grams per hectolitre
Acetaldehyde	3·0
n-Propaldehyde	40·0
n-Butyl alcohol	218·6
Amyl alcohol	83·8
Hexyl alcohol	0·6
Acetic ester	35·0
Propionic, butyric and caproic esters	3·0
Œnanthic ester (about)	4·0
Acetal and Amines	traces.

[The *n* butyl alcohol sometimes found in the fusel oil from brandy (Ordonneau, Compt rend 1886, 102, 217) or grain spirit is probably due to an infection of the yeast by *Bacillus butylicus* or a similar organism. Morin (*l c* 1887, 105, 1019) states that the brandy mentioned above was unsaleable, containing also butyric acid, and that a brandy of good quality analysed by himself contained no *n* butyl alcohol. Elliptical yeast (wine yeast) produced none of this alcohol in the fermentation of 100 kg sugar (*see also* Claudon and Morin, Compt rend 1887, 104, 1187). The absence of *n* butyl alcohol in fusel oil is confirmed by the experience of Kahlbaums Factory (Meyer and Jacobson, "Organische Chemie," I, 1893, 161).]

Morin (Compt. rend. 1887, 105, 1019) distilled 92 litres of pure cognac in Claudon and Morin's apparatus. The first portion of the distillate contained the more volatile bodies, the second consisted of tolerably pure ethyl alcohol, whilst the third contained the higher alcohols and similar bodies. The residue, chiefly water, was tested for free acids, *iso*butylene glycol, and

glycerol. The first three portions were then fractionated, 5 litres of "light alcohol," 55 litres of pure ethyl alcohol, and 3·5 litres of higher boiling compounds being obtained. The last fraction had a strong odour of fusel oil and a burning taste. The water remaining behind was added to that already obtained. The fractions were then re-distilled in Le Bel and Henninger's apparatus. The fusel oil portion, which, after dehydration with potassium carbonate, weighed 352 g., consisted of:

	Grams.
Water	7
Ethyl alcohol	130
n-Propyl alcohol	25
*iso*Butyl alcohol	6
Amyl alcohol	175
Furfural	2
Wine oils	7

The water contained a little acetic and butyric acids and a small quantity of a viscous liquid which distilled undecomposed under diminished pressure, and appeared to consist of *iso*butyl alcohol and glycerol. The residue contained tannin together with substances extracted from the wood.

In the following table are given (1) the compounds contained in 100 litres of cognac, (2) the results of the fermentation of 100 kilos of sugar:

	1. Grams.	2. Grams.
Acetaldehyde	trace	trace
Ethyl alcohol	50,837·00	50,615·0
n-Propyl alcohol	27·17	2·0
*iso*Butyl alcohol	6·52	1·5
Amyl alcohol	190·21	51·0
Furfural and bases	2·19	—
Wine oil	7·61	2·0
Acetic acid	trace	—
Butyric acid	trace	—
*iso*Butylene glycol	2·19	—
Glycerol	4·38	—

n-Butyl alcohol was absent, but furfural was directly detected by the addition of aniline to the cognac, a red coloration being produced in the presence of acetic acid. It will be observed that *iso*butyl alcohol is present only in small quantity, whilst Ordonneau did not record its presence.

In the spirit produced by the distillation of grape products methyl alcohol is usually present although sometimes only in minute proportions; in the product of the distillation of wine Pirani (Annali. Chim. Appl. 1927, **17**, 176) found not more than 0·35%, whilst the distillate of wine press residues contained as much as 4%. He also found that methyl alcohol was present in the rectified products, that from wine containing from a trace up to 0·25%, and that from grape residues 0·54 to 1·90%. Windhausen (Naturwiss. 1929, **17**, 631) and Reif (Z. Unters. Lebensm. 1927, **53**, 168) found similar values. On the other hand, Aschoff and Haase-Aschoff (Z. Nahr. Genussm. 1923, **45**, 209–211) detected no methyl alcohol in genuine brandy, but found that traces were often present in 'marc brandies. Flanzy (Compt. rend. 1934, **198**, 2020–2) found the following methyl alcohol contents (mg. per litre) in various grape and so-called fruit brandies:

Cognac	300–500
Armagnac brandy	600–800
Commercial brandy	1000–2000
"Fruit brandy"	1200–1600
Cider brandy	1000
Pear brandy	660–750
Brandy from cider residues	6000

In addition to the usual method of estimation by determination of the specific gravity of the distillate, the alcoholic strength of a brandy can be ascertained without distillation, but with a close approximation to accuracy, by determination of the specific gravity and of the immersion refractometer reading ($n°$) of the brandy. The relationship between these two values is not affected by the comparatively small amount of extractive matter in solution. Beckel (Z. Unters Lebensm. 1929, **58**, 78) gives the formula $A=1{\cdot}3(KZ/100)\times[30{\cdot}07-(KZ/100)]-6{\cdot}16$, in which A=percentage of alcohol by volume and $KZ=1000+n°-$weight per litre. On the same principle the writer and others have found that for any particular alcoholic strength the value obtained by adding to the reading on the immersion refractometer the difference between 1,000, representing the specific gravity of water, and the specific gravity of the brandy expressed in the same terms, remains unaltered, and tables can readily be prepared correlating factors so obtained with the appropriate alcoholic strengths.

Evaluation.—The analytical data usually relied upon for discriminating between genuine brandies and those blended with neutral spirit are the respective proportions of (*a*) volatile acids; (*b*) aldehydes; (*c*) esters; (*d*) higher alcohols; and (*e*) furfural. The results are calculated in parts per 100,000 of absolute alcohol, *e.g.* in milligrams per 100 ml. or grams per hectolitre. The total amount of the secondary products expressed in this manner is termed the "coefficient of impurities" or preferably the "coefficient non-alcohol." The standard coefficient suggested by Gerard and Cuniasse for genuine brandy is 300, of which not less than 80 should be esters.

The causes which affect the characteristic bouquet of the wine naturally influence the proportion as well as the character of the volatile matters included in the "coefficient" of the brandy. Thus the proportion of the acids and esters is considerably augmented if the wine becomes sour and usually the aldehydes are higher in white than in red wines. von Fellenberg (Mitt. Lebensm. Hyg. 1927, **18**, 337) found that a brandy made from unripe fruit and having an abnormal odour and taste contained mustard oil.

Extent and careful control of distillation are undoubtedly vital factors in the determination of the composition and quality of brandy. If only the early fractions, "produits de tête" which contain the aldehydes and more volatile esters, are taken the flavour of the resulting product is very agreeable and wine-like, whilst the analytical data completely satisfy the usually

accepted standards On the other hand, the later fractions, "produits de queue," containing the higher alcohols and furfural can be greatly improved by the use of dephlegmators. The excess of higher alcohols, furfural, acetic acid, and various obscure substances which, though present only in very small proportion, have a pronounced adverse effect on the odour and flavour, can also be adsorbed by animal charcoal.

In the brandies of Charente and Armagnac the coefficient is usually rather high, but ordinarily in cognacs and *fine champagne* it ranges between 275 and 450, though occasionally it falls considerably beyond these limits. Brandies obtained from wines of the Midi and from Algeria show much wider variations ranging from 25 (indicating strong rectification) to 500. Marc brandies have almost invariably a high coefficient, ranging from 500 to nearly 1,500 and in these aldehydes often form a large proportion.

Attempts have been made to fix minimum and maximum values for the coefficient, but without much success, the former with a view to the detection of the admixture of neutral spirit and the latter to restrict, for physiological reasons, the amount of secondary products. The effect of such limits would be to condemn many brandies which are undoubtedly genuine and even of high commercial value. The French Government in 1904 instituted an enquiry by the Technical Committee of Œnology into the possibility of fixing standards for the total amount of secondary products ("coefficient non-alcohol") of genuine brandy, but the conclusion arrived at was that neither a minimum nor a maximum limit could be recommended owing to the extremely variable character of brandy, not only with respect to the coefficient as a whole, but also in regard to the proportions of the volatile constituents relatively to each other.

The variations disclosed in the published data relating to the composition of genuine brandy and the comparative agreement between these data and those appropriate to factitious products afford some justification to those workers who contend that whilst analytical values are not to be despised, *taste and odour are the most* reliable criteria by which to distinguish the two classes of products. Zellner (Z. Unters. Lebensm. 1927, **54**, 389) and Ruppin (*ibid.* 1929, **57**, 243) support this contention. They are opposed by Buttner and Miermeister (*ibid.* 1929, **58**, 628–635), whilst Graff (*ibid.* 391–393) is of opinion that tasting must occupy a secondary position. In considering the question, regard must be had to the changes which take place when a genuine brandy is "aged," either by efflux of time or artificially, or when one of poor quality or doubtful origin is subjected to an "improving" process. Thus the natural improvement observed in genuine brandies by "ageing" is always accompanied by a rise in the quantity of the secondary constituents due to the formation of oxidation products (aldehydes and acids) and esters, as well as to the concentration due to the loss of alcohol and water. The higher alcohols also tend to increase and furfural to diminish with age. It has been suggested that the mellowness due to age may be imparted to new brandy, making it fit for immediate use, by adding small quantities of old rum, kirsch, syrup of raisins, and infusion of walnut hulls, whilst low wines which have been kept for some months in casks with clear rain-water and a small quantity of strong brandy as a preservative may also be used for a similar purpose. Jarraud (Chim. et Ind., special no, 613–615, May, 1924) has devised a special electrolytic treatment of brandies which effects oxidation, resulting in an artificial ageing in certain respects similar to, but not identical with, natural ageing phenomena.

Physiological Considerations.—The medicinal use of brandy has decreased considerably during recent years, whiskey finding greater favour both as a stimulant and as a hypnotic On the other hand the weight of medical evidence on the question, given before the Commission of Enquiry in 1909, ascribed to the ethyl alcohol and not to the secondary products any beneficial effects to be derived in the treatment of disease. Whilst the inebriating effects of alcoholic liquors may, in the main, be attributed to the common ingredient—ethyl alcohol—the varying effects peculiar to each must be attributed to the secondary products which vary in nature and proportion. There is evidence that the physiological effects of wine and newly distilled brandy are similar, whilst brandy which has undergone a natural process of ageing does not affect the consumer in the same manner or to the same extent. It would appear, therefore, that the higher alcohols which remain practically unaltered in the wine or brandy, whatever the age of the latter, are not the cause of the peculiar effects of brandy. These may be attributed to the other secondary ingredients—aldehydes, esters, and furfural—which undergo considerable change in the transition from wine to old brandy. According to the British Pharmaceutical Codex brandy is of value in the milder forms of diarrhœa and vomiting. By its reflex stimulation of the medulla it acts as a restorative in syncope if given undiluted. It is of value in cases of acute infection; it promotes quieter and deeper *breathing when respiration is affected and* in many cases tends to promote calm and peaceful sleep. F. G. H. T.

BRASS. Yellow alloys of copper and zinc

BRASSIDIC ACID,

$$CH_3\cdot[CH_2]_7\cdot CH.CH\cdot[CH_2]_{11}\cdot CO_2H,$$

is obtained from erucic acid by the action of sodium nitrite, yield 80–90% (Rankoff, J. pr. Chem. 1931, [ii], 131, 293), or of nitrous acid (Holde and Schmidt, Z. angew. Chem. *1922, 35, 502) or* by the action of sulphur and water, sulphur dioxide, or sulphurous acid (Rankoff, Ber. 1930, **63** [B], 2139): erucic and brassidic acids are related as tiglic acid is to angelic acid, and ozonolysis of either gives the semialdehyde of brassylic acid (Holde and Zadek, Ber. 1923, 56 [B], 2052). For further information relative to its configuration and production from erucic acid, *see* Paal and Schiedewitz (Ber. 1930, **63**, [B], 766). It is stable towards air and light.

Brassidic acid crystallises from alcohol in

plates, m.p. 61·5° (Rankoff, *l.c.*, also Holde and Zadek, *l.c.*), b.p. 282°/30 mm.; d_4^{57} 0·8585, n_D^{100} 1·4347; it is less soluble than erucic acid in alcohol and ether; the *anhydride* has m.p. 64° and the *ethyl ester* m.p. 30°–30·5°, *phenyl brassidate* has m.p. 44°, b.p. 285°/12 mm. (Skraup and Beng, Ber. 1927, 60 [B], 942). For *thallous salts* of the acid, *see* Walter (Ber. 1926, 59 [B], 962).

For the p-*chloro*, p-*bromo*, p-*iodo*, and p-*phenyl-phenacyl esters*, *see* Kimura (J. Soc. Chem. Ind. Japan, 1934, 37, 154), these derivatives, and the hydrazides of the acid, provide convenient means of identification of brassidic acid: the hydrazides, prepared by condensing the acid with the appropriately substituted hydrazine, also provide a means of separation of brassidic acid from related fatty acids: the *phenylhydrazide* has m.p. 98°, the *β-naphthylhydrazide*, m.p. 121°–122°, the *αα-methylphenylhydrazide*, m.p. 69°, and the *diphenylhydrazide*, m.p. 106° (Veselý and Haas, Chem. Listy, 1927, 21, 351; Chim. et Ind. 1928 (April), 507).

Esters of *diiodobrassidic acid*, obtained by addition of iodine to esters of behenolic acid (Swiss P. 62968), find application in therapeutics, (U.S.P. 1688100, 1688169). G. F. B.

BRASSYLIC ACID, undecanedicarboxylic acid, $CO_2H{\cdot}[CH_2]_{11}{\cdot}CO_2H$, may be obtained by oxidising behenolic acid, $C_{22}H_{40}O_2$, with fuming nitric acid (Haussknecht, Annalen, 1867, 143, 45; Grossmann, Ber. 1893, 26, 644), or by oxidising erucic acid with nitric acid (Fileti and Ponzio, Gazzetta, 1893, 23 (ii) 393) or with ozone (Verkade, Hartman, and Coops, Rec. trav. chim. 1926, 45, 373). For details of a synthetic method of preparation from undecolic acid involving transformation of *ικ*-undecenoic acid, *see* Krafft and Seldis, Ber. 1900, 33, 3571).

Brassylic acid crystallises in flat needles, m.p. 113°–114°; for X-ray data of the crystals, *see* Caspari (J.C.S. 1928, 3235). It is readily soluble in alcohol and ether, sparingly so in water. The *monomethyl ester*, m.p. 57°–57·5°, is obtained by ozonising methyl erucate and allowing the resulting aldehyde-ester to autoxidise (Noller and Adams, J. Amer. Chem. Soc. 1926, 48, 1074); the *dimethyl ester* has b.p. 170°–210° (Müller, Rölz, and Wiener, Ber. 1934, 67 [B], 295). The *anhydride*, m.p. 76°–78°, is obtained by heating brassylic acid with acetic anhydride (Hill and Carothers, J. Amer. Chem. Soc. 1933, 55, 5023). G. F. B.

BRAUNITE. A manganese mineral classed with the oxides but containing an appreciable amount of silica (8–10%), the formula being $3Mn_2O_3{\cdot}MnSiO_3$ or $4Mn_2O_3{\cdot}MnSiO_3$. The manganese is usually isomorphously replaced by small amounts of iron, calcium, barium, etc. It is generally found in compact masses, but sometimes as tetragonal pyramids, the angles of which are very near to those of the regular octahedron. The crystals possess a perfect pyramidal cleavage. The colour is black with a sub-metallic to metallic lustre. Sp.gr. 4·8; H. 6–6½. The mineral is found in the manganese mines of Sweden; and, with the exception of psilomelane, it is the most abundant of the manganese ores in India (*v.* L. L. Fermor Mem. Geol. Survey, India, 1909, 27). L. J. S.

BRAZILEIN and BRAZILIN *v.* BRAZILWOOD.

BRAZILETTO. An inferior kind of Brazilwood obtained from *Cæsalpinia braziliensis* Linn., growing in the West Indies.

BRAZILITE. A synonym of baddeleyite, native zirconium oxide ZrO_2 (*q.v.*). The same name has also been applied to an oil-bearing rock from Bahia, Brazil. L. J. S.

BRAZIL NUTS. The fruits of *Bertholletia excelsa* Humb. and Bonpl. The principal constituent of the nuts is the oil (*q.v.*), 70% and upwards, which in S. America is used as a food oil.

The nuts contain globulins, an examination of which is reported by Jones, Gersdorf and Moeller (J. Biol. Chem. 1924, 62, 183). Seaber (Analyst, 1933, 58, 575) finds minute amounts of barium as an essential constituent of the ash of the nuts. A. G. Po.

BRAZIL NUT OIL is present to the extent of about 70% in the kernels of the common *Brazil* (Para) *nut*, the seed of *Bertholletia excelsa* Humb. and Bonpl. (Fam. *Lecythidaceæ*).[1] The bulk of the exported nuts is consumed for dessert, confectionery, etc., but a certain amount of oil is expressed in S. America and used for edible purposes, or for the manufacture of fine soaps: technical Brazil nut oil is also prepared to a small extent in Europe from nuts which have deteriorated in transport or storage, so as to be unfit for consumption as food. The fresh expressed oil is pale in colour and has a flavour similar to that of the nuts themselves and deposits a considerable amount of stearin on standing at ordinary temperatures. The iodine value lies between 95 and 106. The fatty acids of the oil consist, so far as is known, of oleic acid (about 45%), linolic acid (about 35%), and saturated acids (about 20%) comprising mainly palmitic acid with minor amounts of stearic acid. The reported presence of very small amounts of myristic acid (Schuette and Enz, J. Amer. Chem. Soc. 1931, 53, 2756) requires confirmation. This is also the case with the acetyl value for the oil, and it seems that we must await further evidence before reaching definite conclusions on these points.

The Brazil nut press-cake can be used as a cattle-food or manure; alternatively it may be treated with solvents for the recovery of the residual oil. Such extracted oil is darker than the expressed oil and only suitable for industrial purposes.

Oil recovered from the parings obtained by slicing off the brown skin (testa) of Brazil kernels had an iodine value of 114·3 (Allan and Moore, J.S.C.I. 1925, 44, 94T). E. L.

BRAZILWOOD. Under the name of Brazilwood certain varieties of the so-called "soluble" red woods are known, the term "soluble" being employed to distinguish them from the dyestuffs of the barwood class, which only with difficulty yield their colouring matters to boiling water. These soluble red woods

[1] Exported *Brazil nuts* occasionally include the very similar *Paradise* or *Sapucaia* nuts from the allied species *Lecythis Ollaria* L. and *L. Paraensis* Hub., etc.

give a bright-red shade with aluminium mordanted fabrics, which in each case is derived from one and the same colouring matter, and all are botanically allied in that they consist of the wood of various species of *Cæsalpinia*. About nine varieties have been employed as dyestuffs, of which the following are the best known:

Fernambuco or *Pernambuco wood* is considered to be the richest in colouring matter, and is the product of the *Cæsalpinia crista*, a tree which is abundant in Jamaica and Brazil.

The true *Brazilwood* is derived from the *Cæsalpinia braziliensis*, and is said to contain only one half the colouring matter which is present in the Fernambuco variety. It is obtained exclusively from Brazil.

Sappanwood is obtained from the *Cæsalpinia sappan*, a tree which is common to the warmer regions of Asia. The so-called *Limawood* is a variety of sappan, and the dyewood imported from the Philippine Islands is an inferior quality of this product.

Peachwood is the product of the *Cæsalpinia echinata* which occurs in Central America and the northern parts of South America.

These woods, which are very hard and of a deep-red colour, come into the market in the form of billets varying in weight from a few pounds up to a hundredweight. If freshly cut, the internal colour of the wood is seen to be light-yellow, but this soon changes to deep red in contact with air.

Some varieties of these woods were employed for dyeing purposes in India long before the discovery of America, and it is stated that when South America was discovered by the Spaniards, in 1500, the northerly portion of the country was named Brazil (from *braza*, fiery red) because this red dyewood was found there in such immense quantities.

Brazilin, the colouring principle of Brazilwood, was first isolated in a crystalline condition by Chevreul (Ann. Chim. 1808, [1], 66, 225) and was subsequently examined by Bolley (Schweiz. polyt. Zeitsch. 1864, 9, 267), and Kopp (Ber. 1873, 6, 446), but it was left to Liebermann and Burg (Ber. 1876, 9, 1883) to determine the exact composition of this substance, and their formula, $C_{16}H_{14}O_5$, is accepted at the present time. To prepare brazilin from the wood itself is a tedious procedure, and the usual method of preparation is from the crude crystalline crusts of the substance which are sometimes deposited from Brazilwood liquor, an intermediate product in the manufacture of Brazilwood extract. The crude substance is best purified by two or three crystallisations from water to which a little sulphurous acid has been added (Gilbody, W. H. Perkin and Yates, J.C.S. 1901, 79, 1396).

Brazilin crystallises in two forms, either as colourless needles containing $1\frac{1}{2}H_2O$, or as colourless prisms with $1H_2O$. It is readily soluble in alcohol and water, and dissolves in a dilute solution of sodium carbonate with a *beautiful carmine-red colour*.

Tetra-acetylbrazilin, $C_{16}H_{10}O_5(C_2H_3O)_4$, colourless needles, m.p. 149°–151° (Liebermann and Burg); *triacetylbrazilin*, $C_{16}H_{11}O_5(C_2H_3O)_3$, needles, m.p. 105°–106° (Buchka and Erck, Ber. 1885, 18, 1139); *brombrazilin*, $C_{16}H_{13}BrO_5$, brown red leaflets (B. and E.); *dibrombrazilin*, $C_{16}H_{12}Br_2O_5$, leaflets (Schall and Dralle, Ber. 1889, 22, 1550); *tetra acetylbrombrazilin*, $C_{16}H_9BrO_5(C_2H_3O)_4$, needles, m.p. 203°–204° (Bushka, Ber. 1884, 17, 685); *tetra acetyldibrombrazilin*, $C_{16}H_8Br_2O_5(C_2H_3O)_4$, m.p. 185° (S. and D.); *tribrombrazilin*, $C_{16}H_{11}Br_3O_5$ (S. and D.); *dichlorbrazilin*, $C_{16}H_{12}Cl_2O_5$ (L. and B.); and *tetrabrombrazilin*, $C_{16}H_{10}Br_4O_5$, fine red needles (B. and E.) have been prepared.

When brazilin is methylated with methyl iodide in the usual manner, it gives *brazilin trimethyl ether* (S. and D., Ber. 1887, 20, 3365; Herzig, Monatsh. 1893, 14, 56; and Schall, Ber. 1894, 27, 525), $C_{16}H_{11}O_2(OCH_3)_3$, prisms, m.p. 138°–139°, which on acetylation yields *acetylbrazilin trimethyl ether*,

$$C_{16}H_{10}O_2(OCH_3)_3(C_2H_3O),$$

m.p. 171°–173° (Herzig, Monatsh. 1894, 15, 140; Schall, *l.c.*).

A convenient method for preparing large quantities of the trimethyl ether by means of sodium methoxide and methyl iodide is described by Gilbody, Perkin and Yates (*l.c.*), and a second method, employed by v. Kostanecki and Lampe (Ber. 1902, 35, 1669), consists in methylating brazilin with excess of dimethyl sulphate and alkali.

The difficulty experienced in fully methylating brazilin is evidence of the presence of an alcoholic group; but the *tetramethyl ether*,

$$C_{16}H_{10}O(OCH_3)_4,$$

m.p. 137°–139°, has been prepared by Schall by treating the sodium compound of the trimethyl derivative suspended in benzene with methyl iodide at 120° (*cf. also* Herzig, *l.c.*). From this substance the following derivatives have been prepared: *brombrazilin tetramethyl ether*, $C_{16}H_9BrO(OCH_3)_4$, prisms, m.p. 180°–181° (S. and D., Ber. 1888, 21, 3014); and *dibrombrazilin tetramethyl ether*,

$$C_{16}H_8Br_2O(OCH_3)_4,$$

m.p. 215° (S. and D., Ber. 1890, 23, 1432).

When brazilin is submitted to dry distillation it gives resorcin (Kopp, *l.c.*), and Liebermann and Burg obtained resorcin by fusing it with potassium hydroxide; Herzig (Monatsh. 1906, 27, 743) also obtained protocatechuic acid in this manner. With nitric acid brazilin yields trinitroresorcinol (Reim, Ber. 1871, 4, 334).

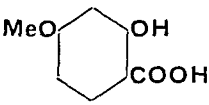
When *brazilin*, the colouring principle, *is* oxidised under suitable conditions, it is converted into *brazilein*, the true colouring matter:

$$C_{16}H_{14}O_5+O=C_{16}H_{12}O_5+H_2O;$$

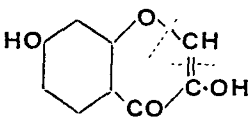
and for this purpose the action of air on an alkaline brazilin solution, of alcoholic iodine (Liebermann and Burg), of potassium nitrite and acetic acid (Schall and Dralle), of nitric acid in the presence of ether (Buchka and Erck), and of sodium iodate (Mayer, Chem. Zentr. 1904, ii, 228) on brazilin solutions have been employed. It was, however, shown at an early period by Hummel and A. G. Perkin (J.C.S. 1882, 41, 367) that brazilein, $C_{16}H_{12}O_5$, is readily obtained

by the atmospheric oxidation of an ammoniacal solution of Brazilwood extract.

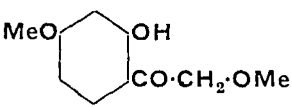
Brazilein consists of minute plates possessing a strong metallic lustre, and by transmitted light a reddish-brown colour. It is very sparingly soluble in all the usual solvents and cannot be recrystallised in the ordinary manner. It is in reality the colouring matter of Brazilwood and possesses strong tinctorial property. Alkaline solutions dissolve it with a deep-red coloration which on standing in air passes gradually to brown. A study of this oxidation by Schall and Dralle led to the isolation of β-resorcylic acid and a *substance*, $C_9H_6O_4$, brownish-yellow needles, m.p. 271°, which gave a *diacetyl* compound, m.p. 148°–149°, and a *dimethyl ether*, m.p. 169°–170°. When the latter was oxidised, β-resorcylic acid monomethyl ether



was produced. Schall and Dralle considered that the compound, $C_9H_6O_4$, was a pheno-γ-pyrone derivative, and this was confirmed by Feuerstein and Kostanecki (Ber. 1899, **32**, 1024) who assigned to it the constitution:



Thus the dimethyl ether, when hydrolysed with sodium ethoxide, gave formic acid and fisetol dimethyl ether:

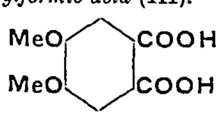


a substance which had already been obtained in a similar manner by Herzig (Monatsh. 1891, **12**, 178) from fisetin tetramethyl ether. Final confirmation of its structure was afforded by synthesis (Pfeiffer and Oberlin, Ber. 1924, **57** [B], 208; and Konermann, *ibid.* 1925, **58** [B], 1947).

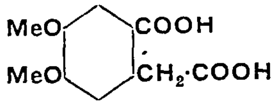
Our chief knowledge of the constitution of brazilin is due to the investigations of W. H. Perkin and his pupils, who obtained important results by the oxidation of brazilin trimethyl ether with potassium permanganate and also with chromic acid.

When brazilin trimethyl ether is oxidised with permanganate it gives, in addition to oxalic, acetic, and formic acids, the following compounds (Gilbody, Perkin, and Yates, *l.c.*; Perkin, J.C.S. 1902, **81**, 1014; Perkin and Robinson, *ibid.* 1908, **93**, 489):

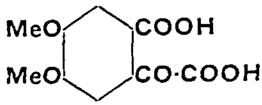
(1) m-*Hemipinic acid* (I), 4:5-*dimethoxy*-2-*carboxybenzylformic acid* (II), and 4:5-*dimethoxy*-2-*carboxybenzoylformic acid* (III).



I.



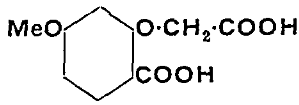
II.



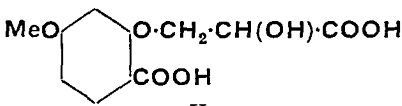
III.

The isolation of these acids was important since they showed that brazilin contains a catechol nucleus and the presence of the two orthohydroxyl groups accounts no doubt in part for its tinctorial properties. Substances (II) and (III) represent intermediate stages in the formation of *m*-hemipinic acid.

(2) 2-*Carboxy*-5-*methoxyphenoxyacetic acid* (IV), and the *acid* (V), the latter, no doubt, being that product of the oxidation which is anterior to the formation of (IV).

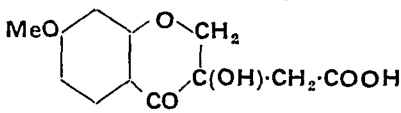


IV.

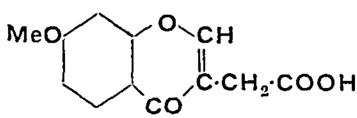


V.

(3) *Brazilic Acid* (VI). When warmed with sulphuric acid this is converted into *anhydrobrazilic acid* (VII), the structure of which was confirmed by the synthesis of its *methyl ester*. A solution of the methyl ester of 6-hydroxy-4-methoxybenzoylpropionic acid in ethyl formate, when treated with sodium, gave the methyl

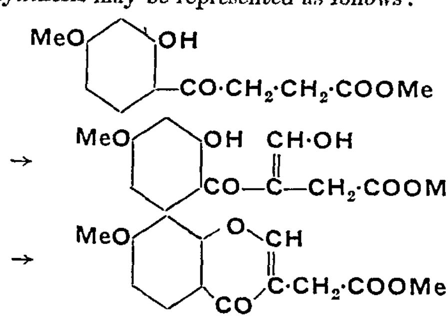


VI.

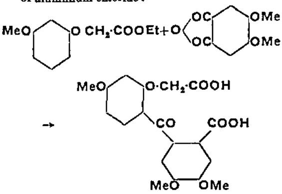


VII.

ester of anhydrobrazilic acid. This interesting synthesis may be represented as follows:



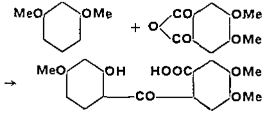
(4) *Brazilinic Acid* (VIII). The constitution of this acid has been conclusively demonstrated by its synthesis, which has been effected by the interaction of *m* hemipinic anhydride with ethyl *m*-methoxyphenoxyacetate in the presence of aluminium chloride:



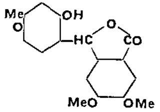
VIII.

A later synthesis of brazilinic acid is recorded by Rây, Silooja and Wadha (J. Indian Chem. Soc. 1933, 10, 617).

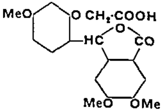
When brazilinic acid is reduced with sodium amalgam it is quantitatively converted into *dihydrobrazilinic acid*, $C_{19}H_{20}O_9$, which at once loses water with the formation of the *lactone* $C_{19}H_{18}O_8$. To synthesise the latter compound, *m*-hemipinic anhydride is condensed with resorcinol dimethyl ether to form 2-hydroxy 4 4′:5′-trimethoxybenzoylbenzoic acid:



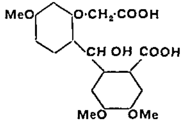
When reduced with sodium amalgam, this acid gives 2-*m*-meconyl 5-methoxyphenol (IX), and this by the action of chloracetic acid and potassium hydroxide is converted into the lactone of dihydrobrazilinic acid (X). Dihydrobrazilinic acid itself is accordingly represented by formula (XI).



IX.

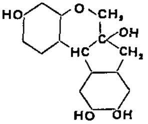


X.

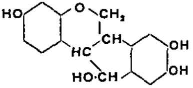


XI.

As a result of this work the following constitution (XII) was assigned to brazilin by Perkin and Robinson (*l.c.*) and is in complete harmony with the facts above enumerated.



XII.



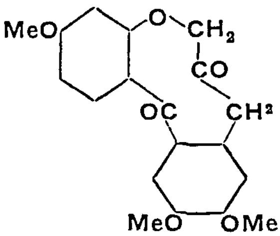
XIII.

v. Kostanecki and his co-workers (*l c*) eventually considered that braziliñ possessed the formula XIII, and such an expression also represented the final conclusion of Herzig and Pollak (Monatsh. 1901, 22, 207; 1906, 27, 743; Ber. 1906, 39, 267) as to the structure of this colouring principle. Such a configuration, however, was untenable, since it did not account for the production of brazilinic acid by the oxidation of trimethylbrazilin (*l c.*), and, indeed, later work has confirmed the correctness of the formula proposed by Perkin and Robinson (*l.c.*).

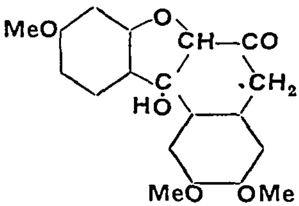
Oxidation of Trimethylbrazilin with Chromic Acid.—When trimethylbrazilin is oxidised with chromic acid it is converted into *trimethylbrazilone* (Gilbody and Perkin, J.C.S. 1902, 81, 1040); this, by further oxidation with permanganate, gives the same products as are obtained directly from trimethylbrazilin by the use of this latter reagent.

The reaction evidently proceeds as follows (Perkin and Robinson, *l.c.*): A disruption of the central linkage of trimethylbrazilin first occurs with the formation of an unstable diketone (XIV) and from this by aldol condensation trimethylbrazilone (XV) is produced. This formula represents trimethylbrazilone as a derivative of both coumaran and tetrahydro-

naphthalene, and affords a ready explanation of the decomposition products of this compound.



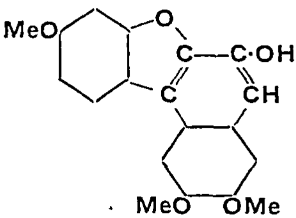
XIV.



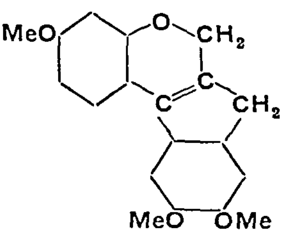
XV.

O-*Triacetylbrazilone* ($+0{\cdot}5H_2O$), m.p. 187° (decomp.), and O-*tribenzoylbrazilone*, m.p. 205° (decomp.), have been prepared (Perkin, Rây and Robinson, J.C.S. 1928, 1513) by oxidising the corresponding brazilin derivatives with chromic acid.

By the action of alkalis, or acetic anhydride and other dehydrating agents, trimethylbrazilone is converted into *anhydrotrimethylbrazilone* (XVI), the formation of this substance being due to elimination of water from the aldol grouping. Anhydrotrimethylbrazilone is thus a derivative of β-naphthol and it possesses many of the properties of this substance, *e.g.*, it is soluble in dilute alkali and such a solution gives with diazobenzene chloride a red azo dyestuff.



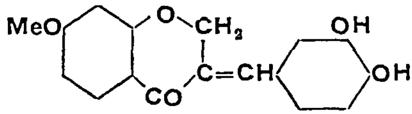
XVI.



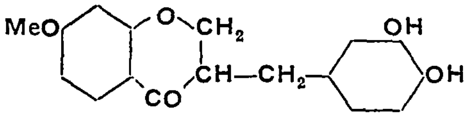
XVII.

When trimethylbrazilone is boiled in acetic acid solution with phenylhydrazine, reduction takes place and *deoxytrimethylbrazilone* (XVII) is produced.

The establishment of the formulæ XVI and XVII for trimethylbrazilone and deoxytrimethylbrazilone respectively is due to the synthetic work of Perkin, Rây and Robinson (J.C.S. 1926, 941; 1927, 2094; 1928, 1504) (*cf. also* Pfeiffer and co-workers, Ber. 1924, **57** [B], 208; 1925, **58** [B], 1947; 1927, **60** [B], 2142; 1928, **61** [B], 294, 839, 1923; 1929, **62** [B], 1242; 1930, **63** [B], 1301; J. pr. Chem. 1931 (ii), **129**, 31). The synthesis of deoxytrimethylbrazilone by the former authors was effected as follows: Protocatechualdehyde condensed with 7-methoxychromanone in acetic acid solution by means of hydrogen chloride gave 3 : 4-dihydroxybenzylidene-7-methoxychromanone (XVIII), from which, by reduction, the saturated *ketone* (XIX) was produced. On methylation in the



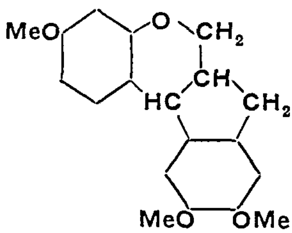
XVIII.



XIX.

usual manner, (XIX) yielded 3-*homoveratryl*-7-*methoxychromanone* and from this, by the dehydrating action of phosphoric anhydride, deoxytrimethylbrazilone, identical with the product from natural sources, was obtained. The structure (XVII) assigned is again confirmed by the fact that on oxidation with ferric chloride deoxytrimethylbrazilone is converted into *iso*brazilein ferrichloride trimethyl ether (*vide infra*).

By reduction with hydrogen and a palladium catalyst (Perkin, Rây and Robinson) deoxytrimethylbrazilone gives the *dihydro*-derivative (XX), and this, when oxidised with chromic



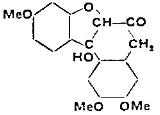
XX.

acid in acetic acid solution, passes into trimethylbrazilone.

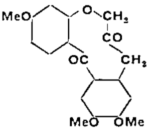
Syntheses of deoxytrimethylbrazilone and trimethylbrazilone have again been effected by Pfeiffer and co-workers (*l.c.*) by methods similar to those detailed above.

The constitution of deoxytrimethylbrazilone as proved by synthesis, led Perkin, Rây and Robinson to suggest the tautomeric system XXI$\rightleftharpoons$XXII$\rightleftharpoons$XXIII for trimethylbrazilone. The phase XXI must be, at least, an inter-

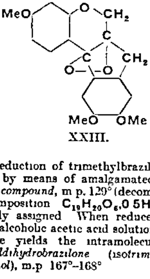
mediate in the formation of α anhydrotrimethyl-brazilone under the influence of aqueous alkalis, whilst XXIII offers an explanation of the remarkable behaviour with phenylhydrazine. Nevertheless, XXI and XXIII can only be related through XXII, which seems to be the most satisfactory single expression of the whole character of trimethylbrazilone which it is possible to select.



XXI.

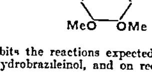


XXII.



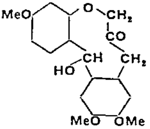
XXIII.

The reduction of trimethylbrazilone in ethyl acetate by means of amalgamated aluminium yields a *compound*, m p. 129° (decomp), to which the composition $C_{19}H_{20}O_6,0{\cdot}5H_2O$ is provisionally assigned When reduced with zinc dust in alcoholic acetic acid solution, trimethylbrazilone yields the intramolecular *pinacol*, *trimethyldihydrobrazilone* (*isotrimethyldihydrobrazileinol*), m.p 167°–168°

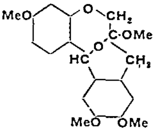


This exhibits the reactions expected of a trimethyldihydrobrazileinol, and on reduction in strongly acid solution gives deoxytrimethylbrazilone (Perkin, Rây, and Robinson).

According to Pfeiffer, Hilpert, and Schneider (J. pr. Chem. 1933 [ii], 137, 227), catalytic reduction of trimethylbrazilone yields the dihydro-compound, *trimethylbrazilonol* (XXIV), a substance which is also obtained, mixed with α- and β-trimethylbrazilopinacones, when the reduction is effected with magnesium and



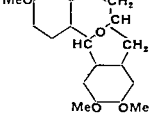
XXIV.



XXV.

acetic acid The α- and β-trimethylbrazilopinacones are reconverted into trimethylbrazilone by oxidation with chromic acid, whilst the β isomeride on further reduction with magnesium in acetic acid gives rise to trimethylbrazilonol. The isomerism of these compounds is attributed to pinacone formation at different CO groups. Trimethylbrazilonol is unimolecular and is oxidised by chromic acid to dihydrobrazilinic acid, with methyl sulphate and alkali it gives a *methyl ether* to which the cyclic formula XXV is assigned on account of its freedom from active hydrogen group.

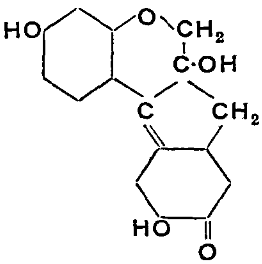
By reducing trimethylbrazilone with sodium amalgam in the presence of alcohol and acetic acid, Pfeiffer and Schneider (J. pr. Chem. 1934 [ii], 140, 9) obtained α-anhydrotrimethylbrazilone, trimethylbrazilonol, β trimethylbrazilopinacone, and the stereoisomerides α and β *trimethyl*allo*brazilin*. α-Trimethyl*allo*brazilin, to which formula XXVI is ascribed, contains no active hydrogen and does



XXVI.

not form an oxime. By the action of acetic anhydride and sodium acetate α- and β-trimethyl*allo*brazilin yield the same *acetyl* derivative, and from this by hydrolysis with dilute acetic acid α-trimethyl*allo*brazilin is readily produced. On warming with alcohol and a little sodium hydroxide solution, the β-isomeride passes quantitatively into the α-compound.

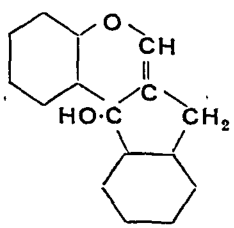
Brazilein.—To brazilein Perkin and Robinson (*l.c.*) assigned the constitution:



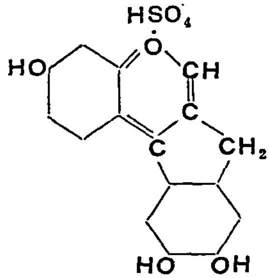
A *triacetyl* derivative, yellow leaflets, m.p. 203°–207° (Schall and Dralle, Ber. 1890, **23**, 1434), and a *trimethyl ether*, which crystallises in two modifications melting at 160° and 178° respectively (Engels and Perkin, Chem. Soc. Proc. 1906, **22**, 132), are described.

When brazilein is dissolved in sulphuric acid and the solution is diluted with acetic acid, minute orange-red prisms of iso*brazilein sulphate* $C_{16}H_{11}O_4{\cdot}SO_4H$, separate (Hummel and A. G. Perkin, J.C.S. 1882, **41**, 367), and this, on treatment with alcohol, gives the basic sulphate $C_{16}H_{12}O_5(C_{16}H_{11}O_4{\cdot}SO_4H)_2$, which crystallises in red needles. Hydrochloric and hydrobromic acids at 100° give iso*brazileinchlorhydrin*, $C_{16}H_{11}O_4Cl$, and iso*brazileinbromhydrin*, $C_{16}H_{11}O_4Br$, and each compound consists of orange-coloured prisms, which are somewhat readily soluble in water, forming a solution which contains free haloid acid. These interesting substances dye mordanted fabrics colours which are entirely different from those yielded by brazilein, and the shades which are produced, especially on calico, somewhat resemble those given by alizarin. From these haloid salts by digestion with silver oxide a substance is produced known as iso*brazilein*, which has the formula $C_{16}H_{12}O_5$ but is totally distinct from brazilein.

According to Engels, Perkin and Robinson (J.C.S. 1908, **93**, 1122), whose paper must be consulted for the detailed account of brazilein and its derivatives, these *iso*brazilein salts are derived from 4:3-indenobenzopyranol (XXVII), and the sulphate is *trihydroxy*-4:3-*indenobenzopyrylium hydrogen sulphate* (XXVIII):

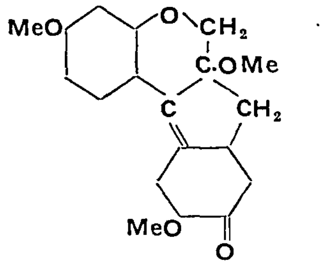


XXVII.

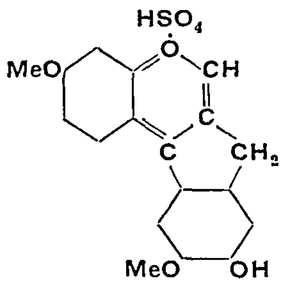


XXVIII.

It was found, for instance, that when brazilein trimethyl ether (XXIX) is treated with sulphuric acid it is converted with loss of methyl alcohol into the dimethyl ether of *iso*brazilein sulphate (XXX). An orthoquinonoid structure is assigned to this and similar oxonium salts.

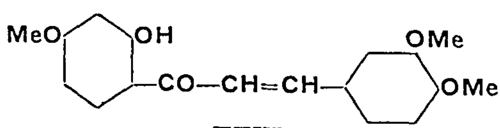


XXIX.



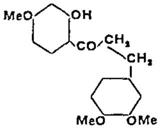
XXX.

Crabtree and Robinson (J.C.S. 1918, **113**, 859), employing butein trimethyl ether, succeeded by very simple means in synthesising *iso*brazilein hydrochloride. By reducing butein trimethyl ether (XXXI), the dihydro (benzylacetophenone) compound (XXXII) is obtained. This by digestion with an excess of absolute formic acid in presence of zinc chloride is

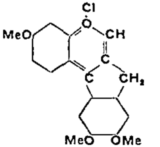


XXXI.

transformed into *iso*brazilein hydrochloride trimethyl ether (XXXIII). With fuming hydrochloric acid at 120°–150° demethylation occurs and *iso*brazileinhydrochloride is produced.

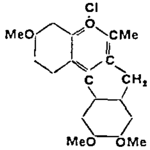


XXXII.



XXXIII.

By the substitution of acetic acid for formic acid in this reaction the corresponding methyl *iso*-brazilein derivative can be obtained:



The synthesis in this manner of a colouring matter so closely allied to brazilin itself by the employment of butein, a yellow dye which exists in the flowers of the *Butea frondosa* (Perkin, J.C.S. 1904, 85, 1459), is of exceptional interest.

The *commercial preparations* of Brazilwood known as Brazilwood extract and Brazilwood liquor are prepared by boiling the ground fresh wood with water and evaporating the decoction thus obtained to various degrees of consistency without access of air, or as rapidly and at as low a temperature as possible, *e g.* in vacuum pans.

Dyeing Properties.—Before dyeing, the logs as imported are rasped to a coarse powder, and this is then usually moistened with water and allowed to ferment for some weeks. This operation is performed in order to increase the colouring power of the wood, and there can be little doubt that a considerable quantity of the brazilin present is thereby oxidised to the colouring matter brazilein. It has been considered by some that the fresh wood contains in reality a glucoside of brazilin, which, under the influence of fermentation, is hydrolysed, but no evidence has been forthcoming in support of this suggestion.

Brazilwood and its allies have lost their importance in dyeing chiefly because of the fugitive character of the colours they yield. In calico-printing, sappan liquor was employed for producing steam-reds and pinks, the mordant used being aluminium acetate or stannic oxalate, separately or combined, together with some oxidising agent, *e g.* potassium chlorate or a copper salt. It also entered into the composition of steam-chocolates and certain steam colours in conjunction with other dyewood extracts. These woods were also much used in the past along with garancine in dyeing the reds, chocolates, and other colours of cheap prints.

In wool-dyeing these woods were applied for the purpose of dyeing reds and various shades of claret and brown, the wool being previously mordanted with alum and cream of tartar or oxalic acid, or with potassium dichromate, in which case other dyewoods, *e.g.* logwood and old fustic, were applied in addition.

In cotton dyeing, *peachwood-red* was formerly obtained by first preparing the cotton with tannin matter, then mordanting with a stannic salt, and finally dyeing with peachwood, sappanwood, etc. Browns were obtained by the use of logwood in addition, with or without a final passage through a ferric salt solution (*nitrate of iron*). These colours are now replaced by others obtained from coal tar.

A. G. P. and E. J. C.

BREAD. The history of bread is lost in antiquity. The drawings which still exist in many Egyptian tombs of early date indicate the existence of the miller and the baker.

Bread is made by baking dough, which is formed by mixing flour or meal with water, and, as a rule, the dough is a fermented one and thus contains carbon dioxide.

The principal ingredient, therefore, in bread is the flour or meal which has been obtained by crushing and grinding the cereal in question. As a rule the ground cereal is submitted to certain purification and sieving processes to remove portions of the husk. Although other sorts of bread are known, the most common form of bread in civilised countries is that made from wheat. In Germany there is, however, still a big demand for rye bread, but this is of a rather different nature from wheaten bread as commonly understood in England. The reason for the particular use of wheaten flour in making bread is that this substance forms a characteristic elastic mass when mixed with water, due to the presence in the flour of a substance gluten (*v.* p. 76). In other words, it forms what is known as dough.

Bread Ingredients.—The principal ingredient is, of course, flour. Wheaten flour consists principally of carbohydrates (70%), proteins ($9\frac{1}{2}$% to $11\frac{1}{2}$%), with moisture (12% to 15%). The major proportion of the protein is represented by gliadin and glutenin (*v.* p. 84) and these two substances have the property of forming with water a colloidal complex which possesses certain elastic properties; these account for the dough-forming power of wheaten flour. The carbohydrates are principally in the form of starch, although some sugar (2% to 3%), the

majority of which appears to be identical with cane sugar, exists. Flour also contains some fat, cellulose and mineral matter. The mineral matter in white flour is small, but the husk of the grain is richer in this respect and, therefore, the lower the grade of the flour the higher the ash.

The next most important ingredient in the making of bread is the yeast, as most bread nowadays is fermented with this substance. Modern practice has indicated the general preference for what is known as distillers' yeast, that is to say, yeast made by the distiller as opposed to the yeast made by the brewer. While brewers' yeast is very active in fermenting sugar, this action is considerably checked by the presence of flour. Jago ("Technology of Breadmaking," 1911, 223) pointed out the toxic action of flour on yeast fermentation, but it would appear that this action is less severe when distillers' yeast is used. For panary fermentation distillers' yeast is not only the most active but is also the most reliable.

Finally, salt is regarded as an essential ingredient in ordinary bread; it toughens the gluten, steadies and checks the fermentation, and is also essential from the point of view of flavour. Various enriching materials, such as milk powders, fats, etc., are sometimes employed.

Principles of Panary Fermentation.—The principles underlying panary fermentation may perhaps be best approached by the consideration of the making of the simplest possible bread with flour, yeast, salt, and water. A dough is made with these ingredients at a temperature suitable for the working of the yeast, normally about 80°F., and in due course the dough begins to rise owing to the liberation of carbon dioxide. This carbon dioxide formation with the subsequent inflation of the dough comes, in the first place, from the action of the yeast enzymes on the sugar which is present in the flour itself. The dough has certain elastic and rubber-like qualities varying with the nature of the wheat used, and it is thus able to retain a considerable proportion of the carbon dioxide which is formed within it and thereby rises or inflates.

It might, therefore, be asked why the fermentation is continued for some time, as is almost invariably the case. The answer is that, in order to get the desired bold, upstanding and evenly aerated loaf, the dough must be what the baker calls "ripe." How soon "ripeness" can be brought about depends upon the conditions, such as the temperature of the dough and the amount of yeast, but it normally takes some time. Bread may be made on a variety of fermentation systems lasting, for example, for periods from as short as 1 hour to as long as 24 hours, but the majority of bread, particularly in England, is made either by a comparatively short process of 3 to 4 hours or by an overnight process of 10 to 12 hours. If the dough is baked before it is ripe, then the loaves will be undersized and will have other defects apparent both to the baker and to the consumer. Similarly, if the dough has become "over-ripe" certain defects will be equally noticeable. The ripening of the dough would seem to be closely associated with changes in the proteins, which, in bread, are principally in the form of gluten. It will thus be understood that these fermentation processes have to proceed until the dough is "ripe" and in the correct condition for baking. Only then will the flour being used give the best possible loaf, as the gluten will have obtained a certain optimum elasticity. At this stage the dough must be kneaded to expel the old stale gas which it contains, scaled off to the desired weight, and moulded into the shape desired for the bread. It is not, however, baked immediately, but again allowed to inflate. During the whole of the comparatively long process of fermentation which has been proceeding in order to ripen the dough, the yeast has been converting the sugar present into carbon dioxide and alcohol. It is, therefore, essential at this critical stage that there should be left in the dough sufficient sugar to allow the finally moulded pieces of dough to inflate again before they are baked. Modern evidence suggests that, in most cases where the fermentation process has been reasonably long, most of the original cane sugar present has been used up and, therefore, a fresh supply of sugar must be available. Broadly speaking, this fresh supply of sugar is in the form of maltose and has been produced from the starch during the process of fermentation by the enzyme diastase present in the flour or other dough ingredients. It is, therefore, essential to ensure that at this period of fermentation, which is generally known as the proving period, there has been sufficient conversion of starch to maltose to provide for the necessary gas production. If insufficient maltose has been formed, there is a grave chance of insufficient inflation at this critical proving period and the loaf will consequently be small, close, and unappetising. If, however, there remains at this stage, or has been produced at this stage, sufficient sugar to cause satisfactory gas production with the subsequent inflation of the dough, a good loaf is likely to result from the baking as the gluten is now perfectly "ripe," and, therefore, the final loaf will be bold and light, have a pleasing even texture, and will be the spongy and easily digestible material desired.

Other systems of charging the dough with carbon dioxide gas are known. Sometimes leaven or sour dough is used instead of ordinary compressed distiller's yeast or the gas is formed by the action of acid on sodium bicarbonate, as is the case when baking powder is used. As will be seen later, the most popular form of bread in Ireland, known as soda bread, is of this type. Modern systems of bread-making will be specifically referred to under the section dealing with bread manufacture.

Chemistry of Breadmaking.—Practically all the bread made in Europe—particularly in England—and America and most other civilised parts of the world is made from wheaten flour. Wheat is widely grown over the surface of the earth, but the flour obtained therefrom varies in its suitability for breadmaking. Very broadly, the strongest flours, that is to say, those that are capable of easily producing the boldest and most pleasing loaves, come from certain districts of the United States and Canada.

Such wheats contain comparatively large quantities of protein which, it has been explained, in flour are mainly in the form of gluten. The gluten is easily obtained when a dough is gently washed, with kneading, under a stream of water. The starch is washed away with the water, but it leaves behind a rubber like mass which consists mainly of protein and is known as gluten The flours which are not so useful for the production of bold loaves are generally called weak flours as opposed to the stronger varieties, and these normally contain smaller quantities of gluten; furthermore, this gluten itself does not have the most desirable physical characteristics In England flour is generally made from a blend of wheats and is thus of medium strength and capable of producing pleasing bread of attractive flavour, as many of the weaker wheats in the blend, particularly those grown in England, have very good flavour.

The flours made from the various wheats containing, as they do, different quantities of gluten of varying quality, have different powers of water absorption in making a dough of the desired consistency. Very approximately dough is made up by adding to the flour rather more than half its weight of water. Although enriching ingredients are sometimes used, it is not generally recognised that if the dough consisted only of flour, yeast, salt, and water, it would be an extremely complex substance. A dough is a complicated colloidal system and dispersed in it is the unicellular living yeast which causes the fermentation and thus introduces constant changes both of a chemical and of a physical nature. The problem of the fermenting dough is a biochemical one.

An ordinary baker's dough, besides containing the starch, some of which is being acted on and gradually converted into various forms of sugar; the gluten, the physical condition of which is regulated by its colloidal condition and thus controls the physical nature of the dough; water in various forms of combination; mineral matter, cellulose, fat, etc., also contains a number of enzymes which bring about important changes. In a dough there are present at least the following active enzymes .

(1) Invertase from the yeast which converts the sucrose present in the flour and/or in the dough ingredients into invert sugar.

(2) Diastase from the flour or other diastatic material added to the dough, such as malt extract, which changes a portion of the starch into maltose.

(3) Maltase from the yeast which converts maltose to dextrose.

(4) Proteoclastic enzymes from the yeast, flour, malt-extract, etc., which tend to soften and break down the gluten.

(5) Zymase from the yeast which converts the dextrose and invert sugar into carbon dioxide and alcohol.

(6) Phytase which liberates inorganic phosphate from phytin.

The fermenting dough is thus a most complicated substance. The most important ingredient of dough is the gluten, which consists mainly of the two proteins, gliadin and glutenin. Gliadin is soluble in 70% alcohol and glutenin in dilute alkali. At one time it was thought that the proportion of gliadin to glutenin in the gluten of flours of different strengths varied and was directly connected with the strength, but recent work does not confirm this theory. Blish (Cereal Chem. 1930, 7, 421) suggests that in all flours there are equal quantities of gliadin and glutenin (v. p. 84) No direct or positive evidence is available as to the mechanism of dough ripening.

It is now recognised that starches from different wheats are variously attacked by the diastatic enzymes present. Mangels (Cereal Chem. 1926, 3, 316) has produced evidence to suggest that the varying powers of flours to produce sugars when autolysed at 27°C. were not due to the varying diastatic powers but to the resistance of the starches in question. For instance, Durum, which produces sugar readily, does not have a highly diastatic extract, but its starch is easily attacked. On the other hand, Kent-Jones and Herd, "Modern Cereal Chemistry," 1927, p. 356, have brought forward evidence suggesting that there are two distinct effects:

(1) The diastatic power of the flour.

(2) The resistance of the starches to enzymic attack.

For example, starch from Durum wheat is distinctly less resistant to diastatic attack than starches of other wheats. On the other hand, the diastatic power of a water extract of Durum flour is greater than the diastatic power of water extracts of other flours, such as Manitoba and English.

The Lintner method of estimating diastatic activity does not give reliable and useful indications as to the behaviour of a flour in baking This is due to the fact that most flour extracts can easily convert soluble starch into sugar, but have varying powers of converting insoluble starch into the soluble variety.

With respect to the susceptibility of wheaten starch to diastatic attack, it is now known that the system of milling, the pressure exerted in the milling process, the nature and speed of the rolls, etc., have an effect.

As panary fermentation proceeds the dough increases in acidity, and at one time it was thought that for the best results a p_H of 5·0 had to be reached. The importance of hydrogen ion concentration in bread-making, however, has been too much stressed. Fisher and Halton, of the Research Association of British and Irish Millers, have investigated the effect of hydrogen ion concentration and buffer value on the baking quality of flour, and their conclusions are diametrically opposed to those of Jessen-Hansen who had advanced the point of view of the necessity of the dough ripening to a p_H of 5·0, if the best volumed bread was to be obtained. Fisher and Halton (Cereal Chem 1928, 5, 445) state that hydrogen ion concentration is not a factor of great importance in bread-making and contributes little or nothing to loaf quality. They state:

"Extensive baking tests have been carried out with a great variety of flours over wide ranges of H-ion concentration (from p_H 7·80 to 4·20) and varying periods of fermentation.

The results of the work appear to confirm the conclusion reached in an earlier investigation that H-ion concentration is not a factor of great importance in determining dough or loaf quality. Alterations of H-ion concentration brought about in doughs by additions of acid several times greater than those brought about by prolonged over-fermentation appear to have singularly little effect on dough or loaf characters. Moreover, the effects observed are not always in the same direction, *e.g.* slight improvement of some characters and slight damage to others may result from increased H-ion concentration."

Their conclusions seem to be well substantiated and to have been generally accepted.

It will readily be understood, therefore, that the fermented dough when it enters the baking oven is not simply the same dough as was first made but is now filled with gas, and has undergone important physico-chemical changes.

When the baking operation takes place, the changes are still more marked and consequently more obvious. A certain proportion of the starch becomes gelatinised and consequently more highly dispersed from a colloidal aspect, while the swollen and hydrated proteins become coagulated. This complex mixture is permeated with minute bubbles of gas which are responsible for the aeration of the loaf and its characteristic internal structure. What is known as the texture of a loaf is a matter of great importance to the baker. For English bread, the crumb must not be holey but should be what is called evenly vesiculated. If the gas bubbles held in the delicate meshwork of gluten threads, etc., break from their immediate surroundings and coalesce, too coarse a texture may result and, in extreme cases, holes may be formed.

During the baking process dextrin is produced on the crust by the action of the heat and steam on the starch, and this is largely responsible for what is known as the glaze or bloom on the crust. A proportion of the residual sugar is caramelised. The temperature of the oven soon checks the enzymic actions which have been progressing during fermentation and the loaf normally jumps to its full size in 10 to 15 minutes after placing the dough in the oven. The strain on the network of hydrated proteins in holding the expanding gas is considerable, but it is essential for the production of good bread that the network should be strong enough to resist this strain, and in this way a bold loaf of pleasing texture is produced.

The miller's problem, therefore, is to select such wheats as will blend well with one another to produce a satisfactory flour for breadmaking. One wheat may have a small quantity of gluten and another a large quantity of gluten; together they balance reasonably nicely in this respect. Another wheat may tend to produce a flour the gluten of which is too flowy; this should be blended with a wheat the gluten of which tends to be stable. If the gluten is either too stable or too flowy the best results cannot be obtained, but by suitable blending and care in milling the best use can be made of the different wheats.

The baker has to recognise the particular characteristics of the flour and its behaviour in the dough so as to adjust his fermentation process to get the best result. For example, the gluten of a weak flour breaks down too rapidly if the fermentation is at all long and severe and, therefore, such flour gives the best bread when worked on a short, quick process. On the other hand, certain very strong flours definitely require a large amount of fermentation to mellow them to the correct degree of ripeness and, therefore, must be given a reasonably long fermentation to get the best results.

The chemistry of bread has, therefore, been principally directed towards:

(1) The characteristics of flours from different wheats.
(2) The effect of varying methods of fermentation.

It is essential that the flour should have a reasonable amount of protein or gluten and this in a good condition, so that it is able to make a dough of satisfactory physical characteristics. In other words, besides the quantity of protein or gluten present, there is the all-important matter of its quality, and valuable work has been done in this connection by Wood and by Hardy. Wood (J. Agric. Sci. 1907, 2, 139, 267) attempted to find some connection between the chemical constituents of flour, and more especially of gluten, and the strength or baking behaviour of flour. Wood was one of the first to differentiate clearly between the two important factors:

(1) The gas-producing power of the flour.
(2) The gas-retaining power of the flour when made into the dough.

It was the quality of the gluten in relation to the gas-retaining power that chiefly interested him, and he was one of the earliest investigators to examine gluten from a colloidal point of view. He examined the influence of acids on glutens observing what happened when gluten was suspended in different strength of acid. For example, $N/100$ hydrochloric acid caused a rapid disintegration of the gluten, but when $N/10$ solution was used the gluten became tougher and less sticky. Wood and Hardy (Proc. Roy. Soc. 1909, B, 81, 38) suggested an electronic theory to account for the various changes, and this work was continued by Hardy (Rep. Brit. Assoc. 1909), who stated that gluten from the strongest and best wheat had of itself neither pleasing elasticity nor toughness. These useful properties, as far as breadmaking is concerned, were merely impressed upon it by the surrounding conditions, which in the main were the presence of certain electrolytes. Similar work was done by Upson and Calvin (J. Amer. Chem. Soc. 1915, 37, 1295–1304; Nebr. Agr. Exp. Sta. 1916, Bull. 8). Sharp and Gortner (Minn. Agr. Exp. Sta. 1923, Tech. Bull. 19) and Sharp, Gortner and Johnson (J. Phys. Chem. 1923, 27, 942–947) continued work on the colloidal nature of flour proteins, but the most recent work is by Bungenberg de Jong and Klaar (Cereal Chem. 1929, 6, 373; 1930, 7, 222, 587; 1931, 8, 439; J.S.C.I. 1933, 52, 391T). These papers mainly deal with the colloidal aspect of gluten and its two main constituents, gliadin and glutenin,

and with the electric charges on the two proteins. A study was made mainly by viscosity and turbidity into the various colloidal complexes formed by these two proteins at various values of p_H. Kent-Jones ("Modern Cereal Chemistry," 1927, p 133) has suggested that for good strength the flour proteins must have a certain degree of dispersion, and that unsatisfactory protein characteristics indicate a colloidal nature on either side of this mark. This "optimum coagulation theory," as it has been termed (Geddes and Goulden, Cereal Chem. 1930, 7, 527), certainly fits in with a number of facts, and has received confirmation by the work of Harris on the peptisation of flour proteins (Cereal Chem. 1931, 8, 47, 113, 190, 496). Other investigators in America have followed up the work of Harris, namely, Geddes, Larmour, etc., and much of this work has been reported upon in Cereal Chemistry for the years 1930–1931, and some also in the Canadian Journal of Research.

Berliner and Koopman (Z. ges. Muhlen. 1929, 6, 57) have utilised the swelling power of gluten to evolve a test for wheat and flour quality.

Flour contains varying quantities of phosphatides and their effect on the baking quality has been investigated by Working (Cereal Chem. 1928, 5, 223) and Sullivan and Near (*ibid.* 103) This work has not so far been extended, although its importance is obvious.

That part of the chemistry of bread which deals with the varying methods of fermentation is unfortunately still very vague in spite of work done by the Research Association of British and Irish Millers. There is a marked difference between bread made on a short and on a long fermentation system, but little scientific data has been collected. Bread produced by the longer system is, of course, often definitely sourer and to some people too sour. In Scotland, however, such bread is appreciated and ordinary bread considered to be without taste.

There is little precise knowledge as to the changes in the gluten which take place during fermentation. It seems unlikely that the fermented dough is the same as first made but charged merely with carbon dioxide, as some authorities think. The fact that there is a definite difference between long fermentation bread and short indicates that certain changes must take place. During fermentation there appears to be an increased mellowness of the gluten.

During panary fermentation there is a definite loss of weight, as certain dough solids are converted into carbon dioxide, etc., and thus lost. The loss in weight may be as much as ½ to 2%.

Dough Testing Apparatus.—A fairly recent development in cereal chemistry is the use of dough-testing apparatus. A baker will prefer one flour to another because its dough has more pleasing physical characteristics, which he knows normally result in the production of better bread. The chemist should obviously be able to measure these physical properties with some degree of accuracy, and for this reason various machines have been devised. Although a number of such machines have been made, perhaps the most successful have been the Chopin Extensimeter and the Brabender Farinograph. In the Chopin Extensimeter a sheet of dough of definite thickness is blown by air pressure into a bubble and the forces in play, the work done on the dough and a number of other facts are recorded mechanically. The test, when properly standardised, gives much valuable information as to the physical characteristics of the dough and indicates why one dough is preferred by the baker to another. The other apparatus, the Brabender Farinograph, measures the force required to turn mixing arms in the dough. The continual mixing, which is at high speed, gradually breaks down the dough and, from the nature of the force required as the experiment proceeds, an indication of the value of the properties of the dough for ordinary bread making can be obtained.

Such dough tests, although by no means perfected and still capable of improvement, throw a great deal of light on the usefulness of certain flours for baking and on their colloidal structures.

Manufacture of Bread.—Most bread, particularly in England, is made with yeast, flour, salt, and water, and occasionally with additions of enriching materials such as milk powder, fat, etc. Either short doughs (*e.g.* 2 to 5 hours) or long doughs (*e.g.* 6 to 10 hours) are made, the method employed depending on its suitability for the business. Naturally a long dough has a comparatively small quantity of yeast and a fairly low temperature, while a short dough certainly has a higher percentage of yeast. Practically all bread is made with compressed distillers' yeast. In Australia, however, spontaneous yeast is still used, as distances are great for transportation of fresh material. This spontaneous yeast (commonly known as *spon* yeast) may be made as follows:

16 gallons water.
1 lb. hops.
1½ lb. bran.
6 lb. crushed malt.
9 lb. sugar.
9 lb. flour.
40 lb. potatoes.

The hops and the bran are boiled together for 25 minutes, strained into a tub, and cooled down to 160°F. The malt is then stirred in and allowed to stand for 3 hours; the liquid is strained off and the residue well squeezed. The steamed potato pulp is added to the liquor which is cooled down to 85°F.; the sugar and flour are then added, stirred well, and the stock or old "spon" (3 pints) introduced. Dough temperature, 80°F.

In Scotland, especially for Scotch batch bread, *barms* are still used. Although both compound and virgin barms are sometimes employed, the more usual is the Parisian barm. It contains the following ingredients:

$\left.\begin{array}{l}\text{2 lb. crushed malt}\\ \text{5 quarts water at 165°F.}\end{array}\right\}$ mashed together.
Water to make 5 quarts strained liquor at 125°F.
17 lb. flour.
9 quarts water at 212°F.
2 quarts old barm.

No hops or salt are used in producing this barm nowadays. The malt and water at 165°F. are mashed for at least $3\frac{1}{2}$ hours in the same way as for compound barm but without the hops. The liquor, when pressed out, is made up to the initial quantity with water at a temperature sufficient to secure 125°F. in the total liquor. The flour is now stirred in by hand and immediately afterwards boiling water is stirred in to gelatinise the flour starch. The "scald" is now allowed to cool spontaneously to 76°F. for, say, 16 to 18 hours, when the "store" or old barm is stirred in. The barm, when "stored," is left to ferment for three days (72 hours), but it may be used on the fourth day and even on the fifth day after storing. The period of 72 hours is said to result in the sweetest bread and it is common practice to make Parisian barm twice a week. The barm, if kept cool, will not deteriorate quickly with age.

The comparative strengths of yeast and barms are as follows:

1 lb. of distillers' yeast is equal to about:

6 quarts of compound barm, or
9 quarts of virgin barm, or
$7\frac{1}{2}$ quarts of Parisian barm.

It is, of course, possible to make straight doughs with barm in place of distillers' yeast, although a rather longer time is necessary.

When the sponge and dough system is employed only a proportion of the flour and water together with all the yeast are first used and when the fermented sponge is ready it is broken down with the remainder of the water and doughed up with the remainder of the flour. The main quantity of salt is added at the doughing stage. This method is said to give particularly good flavoured bread and to enable it to be made with a minimum amount of yeast. With the ordinary half sponge, half the amount of water is used in making the sponge and, after it has been allowed to ferment, the remainder of the water and flour, and all the salt are added.

In Scotland the quarter sponge system is particularly popular. In this the quarter sponge, which is usually set at a low temperature, such as 72°F., and is made very stiff, ferments from 14 to 15 hours. The flour required for this purpose has to be very strong, such as Manitoba. At the end of this time it is broken down with more water and is then in the state of a thin sponge. After about 60 to 70 minutes the final dough is made. Full details of this and other methods will be found in text-books on breadmaking, such as Jago's "Technology of Breadmaking," London, 1911, Kent-Jones' "Practice and Science of Breadmaking," and Bennion's "Breadmaking," London, 1929.

Leaven, that is to say sour dough, is not used much in England, but a large proportion of the bread in the Strasbourg district and other parts of the Continent is made in this way. For the making of rye bread, sour dough or leaven is almost invariably used.

In Ireland the proportion of the normal yeast bread eaten is comparatively small, as most of the flour (probably 60%) is made into bread without yeast fermentation. For this purpose a soft flour is used and a dough is made with a little sodium bicarbonate and sour butter milk. The acid of the milk liberates carbon dioxide, which gives the necessary aeration on cooking. Naturally, no fermentation time is required. A typical formula would be as follows:

$1\frac{1}{2}$ lb. flour.
$\frac{1}{3}$ oz. salt.
$\frac{1}{7}$ oz. sodium bicarbonate.
Approximately 1 pint buttermilk or sour milk.

In order to ensure that there is sufficient acid the flour often contains 1 to 2 lb. per sack of acid calcium phosphate.

At one time aerated bread made by injecting carbon dioxide into the dough was popular, the process having been brought out by Doctor Daughlish in 1859. The bread, however, is inclined to be insipid and such tasteless bread is not appreciated by all people.

A typical 4-hour straight dough process as used in England would be as follows:

1 sack (280 lb.) flour.
2 lb. yeast.
4 lb. salt.

A malt addition would be used in certain circumstances and particularly if the flour happened to be low in diastatic activity. The dough would be made to a temperature not exceeding 80°F. and allowed to ferment for about $2\frac{1}{2}$ hours. It would then be thoroughly knocked back to get rid of stale gas and to drive the yeast into fresh feeding places. The dough would ferment for a further half-hour and would then be scaled off. After a short recovery period it would be moulded up and given its final proof, so as to be ready for the actual baking. In a 10-hour or overnight process only about 10 to 12 oz. of yeast per sack would be required (dough temperature approximately 78°F.) and the knocking back, which is particularly important in such a long system, would take place about an hour before the dough is scaled off.

Bread is either made in comparatively small quantities by the small baker or is produced on mass production lines in automatic plant. Even the small baker to-day rarely mixes his dough by hand but employs a dough-mixing machine. The "knocking-back" of the dough is still, however, often done by hand, although the modern open pan dough-mixer enables this to be done by machinery. The small baker normally divides and scales off by hand and the dough is hand-moulded. With skilled workers excellent bread can thus be made. The secret of successful breadmaking lies in making cool doughs and using plenty of yeast. Also thorough and proper "knocking-back" of the dough is desirable.

In an automatic bakery not only is the dough-making and the "knocking-back" automatic, but the dough is divided and scaled off by dividers and even the preliminary and final mouldings done by moulding machines. The baking is carried out in large automatic ovens which are either of the travelling sole or of the swinging tray type. Finally, the bread is cooled

in automatic plants and, when cooled, is wrapped

The smaller bakeries use either peel ovens or draw-plate ovens. In the peel oven each loaf is put in more or less separately by hand on a flat wooden shovel called a peel. In the drawplate oven the sole itself draws out. It can, therefore, be loaded rapidly and pushed back into the oven.

Various methods of heating ovens are employed, many of the small peel ovens are internally fired, that is to say, the fire is built up inside the oven and is removed before baking. The oven becomes sufficiently hot, being built of heavy brickwork, to retain the heat for the baking process. Other types, and particularly drawplates, are heated by steam tubes. The tubes are hermetically sealed and contain water. One end enters or forms part of the furnace and the other end of the tube enters the baking chamber. Naturally a tremendous pressure is evolved in these tubes, which have to be very carefully made. If ill used, however, a burst is not unknown. The steam tubes can be so arranged as to give uniform heating and the system has been employed for travelling ovens. These can be fired either by coke, gas, or oil. Electrically heated ovens are occasionally employed, especially with small types.

Bread Faults.—Although certain flours are capable of easily giving better breads than others, yet much of the criticism of bread is due to faults in bakery technique. Bread for England should have an even texture and a bright crumb. The crust must not be either too hard or too soft and normally a fairly large loaf volume is wanted. As explained in the section on the Principles of Panary Fermentation, the dough must be ripe when baked. Much faulty bread is produced by baking the dough in an incorrect state of ripeness, either under ripe or over ripe. An over ripe dough is generally "short" and "snappy," particularly when being moulded. The crust of the loaf is ragged and the colour likely to be pale. The crumb is inclined to be greyish and dull and the loaf volume small. The crumb will tend to be very crumbly and the loaf stales quickly. Under ripe dough tends to be flowy and produces a loaf with too red a crust, with a close, heavy and rather dull texture and of small volume.

A frequent cause of complaints in bread is holes, and these are mainly caused through poor and incorrect moulding. Holes may also be brought about by other causes, such as the irregular dispersion of the yeast in the water, the use of too much dusting flour or cones, and, particularly, bad oven practice. Cottage loaves are bound to have holes if incorrectly "bashed." When holes are giving trouble attention should be directed to:

(1) The moulding.
(2) The fermentation.
(3) Proof and oven procedure.
(4) Nature of the flour, particularly with respect to seeing if its diastatic capacity is on the low side.

Another frequent cause of trouble is the presence of dough-like streaks. These may come with any flour, particularly if, when it is divided, it is allowed to become chilled; undoubtedly those flours which tend to have high diastatic capacity are most likely to give trouble.

Bread Flavour and Nutritive Value.—Considerable attention has been paid in recent years to the flavour of bread, as it is claimed by some people that modern bread is lacking in flavour. Nothing ensures satisfactory flavour in bread so well as the use of cool doughs, plenty of yeast and salt, and a correct degree of fermentation. The tendency often is to restrict the quantity of yeast and, in an endeavour to get the doughs ripe in too short a time, to increase the temperature. This generally results in poor bread. Undoubtedly the type of loaf is not without influence on flavour. The most flavoury bread is generally that having a good crust, and the modern demand for tin and sandwich loaves must necessarily react in reducing the bready flavour, which is often appreciated and nowadays missed. Visser't Hooft and de Leeuw (Cereal Chem. 1935, 12, 213) have suggested that bread flavour is due to the presence of acetyl methyl carbinol which oxidises to diacetyl, but Maiden (J.S.C.I. 1936, 55, 143) was unable to confirm this.

It is naturally important to make a bread as attractive as possible in view of the fact that it is probably one of the cheapest and most nutritious of all foods. In general, more calories can be bought for a penny as bread than as any other common food, while the value of the vegetable proteins in the bread is not to be despised. White bread is, of course, generally deficient in vitamin B, and for this reason brown bread is sometimes advocated. In view of the fact, however, that bread is commonly eaten with other articles of the diet, it does not seem logical to attempt to make bread a complete food, and the substitution of brown bread for white is not always helpful. Germ breads are certainly richer in vitamin B than ordinary wholemeal breads, which contains so much of the indigestible husk of the wheat grain. The slight aperient action of wholemeal, however, is helpful with certain people of sedentary habits.

Rope.—Reference should be made to the occasional presence of this disease in bread. Fortunately, this is not dangerous to health, but ropy bread is extremely unpleasant. If bread is kept in a warm, damp place for two or three days it may develop rope. It acquires first of all a slightly fruity smell, which rapidly becomes more pronounced and unpleasant, while the crumb becomes soft and sticky. The trouble is usually brought about by the bacterium *B. mesentericus vulgatus*.

The usual precaution is to cleanse the bakehouse by thorough washing, lime-washing the walls, etc., and scrubbing the tables and troughs with vinegar. *B. mesentericus vulgatus* cannot thrive if the p_H is as acid as, or more acid than, 5.0. When there is danger of rope, therefore, about 2 lb. per sack of acid phosphate or a pint of vinegar per sack is often incorporated in making the flour into dough and care should be taken to see that fermentation is vigorous. Above all, the bread should be cooled as rapidly as possible and kept cool. Rope naturally

appears in large loaves rather than small loaves as the former cool so much more slowly. The pioneer work in England in investigating rope was done by Watkins (J.S.C.I. 1906, **25**, 350), and a method for the determination of the number of rope spores in flour, and factors affecting the growth of *B. mesentericus vulgatus* in bread are given by Amos and Kent-Jones (Analyst, 1931, **56**, 572).

Flour Treatment.—Reference should also be made to the fact that in England, Germany and America, but not in France and certain other countries, the treatment of flour with minute traces of chemicals is often carried out, the object being to improve either the colour or the baking value of the flour.

Only those substances which are completely harmless in the quantities needed are employed, but the use of certain chemicals and treatments enables the European miller to use larger quantities in his blend of the weaker and flavoury European wheats and still to obtain sufficient strength in his flour. The practice was investigated by the Departmental Committee of the Ministry of Health (Report of the Departmental Committee on the treatment of flour with chemical substances, H.M. Stationery Office) and their report was published in 1927. Although not generally in favour of the practice, they realised that there was little or no evidence to show that these additions were harmful, but they suggested that the use of chlorine, nitrogen trichloride and benzoyl peroxide should not be allowed. They had little objection to phosphates and persulphates, but recommended that if, as had been suggested, flours could be improved by physical processes, such as heating, this would be the best method of dealing with the problem. This report has not been acted upon and at the present moment, for example, a large proportion of flour is being treated with nitrogen trichloride.

Commercial plants for the improvement of flour by heating are also in operation in a large number of mills, and various patents have been taken out (B.P. 263897, 338603, 300291, 300537). There have been a number of scientific investigations into the effect of heat upon flour, some of which have been reported upon in "Modern Cereal Chemistry." Of recent years Herd (Cereal Chem. 1931, **8**, 1, 145) and Geddes (Canad. J. Res. 1929, **1**, 528; 1930, **2**, 65, 195) have made valuable contributions to this subject.

In general, certain substances are used for the bleaching of flours and others for the improving, that is to say, for increasing the baking qualities; some substances also have the dual action. One of the most popular, although one of the oldest, flour bleachers is nitrogen peroxide, which is usually produced by passing air through a flaming electric discharge. The treatment of flour with nitrogen peroxide was patented as early as 1901 by John and Sydney Andrews, although the gas was then produced chemically. In 1903 the Alsop patent was granted, the active principle of which was again nitrogen peroxide but made more conveniently by passing air through a flaming discharge of electricity. The proportion of air so affected is, however, small. This means that the residual nitrite in the flour is practically negligible, usually about two to three parts per million.

Flour contains two to three parts per million of carotene and this is responsible for the yellow tint in flour. By oxidation (and also chlorination) the yellow tint of the carotene is removed, but it should be noted that ordinary bleaching agents cannot remove the dullness of low-grade flour which is due to the presence of minute specks of bran powder. Bleaching involves only the removal of the yellow tint and does not really alter the appearance of a low-grade flour and make it resemble that of a high-grade one.

A more recent bleaching agent is benzoyl peroxide [$(C_6H_5CO)_2O_2$]. This is a powder and the bleaching action does not normally become effective until it has been mixed into the flour for at least 24 hours. The quantity used is extremely small, probably in the region of 1 part of pure benzoyl peroxide to 50,000 parts of flour.

Chlorine and nitrogen trichloride are also popularly used, the latter more especially. The normal treatment for the latter is in the region of 2–3 g. per 280 lb., which is approximately 1 part to 40,000 or 50,000. This not only bleaches the flour by taking away the yellow tint of the carotene, but it also has a marked improving action on the baking qualities. The flour tends to become stronger, to have more pleasing and elastic dough-like qualities, and to produce bolder and better textured bread.

With respect to those substances solely used as improvers, the best known are perhaps acid calcium phosphate, which has to be used at the rate approaching 1 lb. per sack of 280 lb. of flour, ammonium persulphate, and potassium bromate. These last two substances have largely displaced acid calcium phosphate, which was used earlier. Ammonium persulphate used at the rate of 1 part in 20,000 gives a marked improvement to the dough and to the resulting bread, and the same is true of the use of potassium bromate, which can be employed at the rate of 1 part in 50,000. There has never been any serious evidence that the use of these minute traces of chemicals which improve bread is in any way deleterious to health, although it has to be borne in mind that they are definitely prohibited in certain countries and are not looked upon favourably by all authorities.

Staling.—The phenomenon of the staling of bread is well known and in recent years there have been numerous investigations into factors influencing and controlling it. The principal work in this field has been done by Katz (Z. Electrochem. 1913, **19**, 633; Z. physiol. Chem. 1915, **95**, 104, 136, 147), who has made many contributions over a number of years. It is now, of course, thoroughly established that staling is not related to loss of moisture, as it will occur even when bread is placed in a damp atmosphere. Ostwald (Kolloid-Z. 1919, **25**, 26) regards staling as a simple case of syneresis—the phenomenon under which, in course of time, all gels separate into two phases, one solid and one liquid. This suggestion does not find favour with Katz, who associates staling with starch retrogradation. Most investigators are of the opinion that the change seems to concern

the starch gel more than the protein gel and that the amount of water soluble polysaccharides is smaller with stale bread than with fresh. Useful guidance on this question generally has been obtained by a study of the X-ray diagrams of starches.

A general survey of this subject was made by Katz in R P Walton's book "A Comprehensive Survey of Starch Chemistry," 1928, Chemical Catalogue Co

This matter has also been investigated by Washington Platt (Cereal Chem 1930, 7, 1) and he is doubtful whether staling can be entirely attributed either to syneresis or to retrogradation of the starch. Amongst other tests, Platt suggests that measurement of staling can best be determined by the rate of change of the compressibility of the crumb and proposes an apparatus to do this Karacsonyi (Cereal Chem 1929, 6, 241) prefers to measure staleness by the viscosity of crumb suspensions Stale bread is not as viscous under his conditions as fresh bread Katz, for a general test, prefers the reading of the volume of the crumb when in water The crumb is shaken up in water which contains some toluene to prevent fermentation and the sediment allowed to settle for various periods The volume of the sediment is considerably larger for fresh bread than for stale

No very striking practical proposals have been made with the idea of preventing staling The suggestions to keep the bread either very cold or very warm are not practical, and the only substances, such as aldehydes, which seem to delay the onslaught of staling cannot be used because of taste On the other hand, the technique of breadmaking certainly influences the rate of staling Incorrect water adsorption and incorrect fermentation tend to produce breads which stale unduly rapidly The dough must not be made too warm or too tight and certainly should not be over proved Oils and fats tend to delay staling and the same may be said of some malt additions Certain specialty breads certainly keep fresh longer than normal bread Possibly the full hydration of the gluten has something to do with the matter, as there is a growing feeling that staleness is, partly at any rate, associated with an interchange of water from the starch to the gluten of the bread

Analytical Methods.—For analytical methods concerning flour, bread and cereal products generally, reference should be made to Kent Jones' "Modern Cereal Chemistry," and to "Cereal Laboratory Methods" published by the American Association of Cereal Chemists (1935 edition)

Moisture.—The control of moisture in milling practice and knowledge of the moisture contents of flour-mill products generally, bread, etc, are naturally important. Numerous methods for this determination exist, but in general the loss of weight shown by the substances when dried in ovens at about 100°–110°C. is employed. Much depends on the type of oven, the temperature, and the actual technique employed. A moisture content of 15% in one type of oven might be given as 16½% in another type. It is, therefore, necessary to remember that moisture contents are only relative.

It is often important to be able to obtain moisture contents of such materials as wheat and milling products quickly. Blish and Hites (Cereal Chem. 1930, 7, 99) have described a method in which the moisture content of flour can be determined fairly accurately in 5 minutes by the use of calcium carbide A 1 g sample of flour is mixed with calcium carbide in a closed system connected with a mercury manometer, and the pressure exerted by the acetylene gas produced is proportional to the quantity of moisture present. Although some of the flour moisture is non-reacting, this appears to be reasonably constant, and hence the apparatus can be standardised.

The Carter Simon oven is in fairly general use in a large number of mills, and by utilising a temperature of 155°C. in a specially designed chamber, the moisture content can be determined with only 15 minutes' heating Actually the samples are usually tested in triplicate, each sample gradually being pushed through the oven as new samples enter. It is, therefore, possible to make an accurate determination in about half an hour This method has been favourably reported upon by Coleman and Dixon (Cereal Chem. 1926, 3, 419)

There are also a number of electrical moisture testers available. The Burton Pitt apparatus (Canad J Res. 1929, 1, 155) and the German D K apparatus are wired with radio circuits and make use of an alternating current of high frequency. The strength of the current is altered when damp materials are inserted into the condenser on account of differences in the dielectric constants and these are related to the moisture content of the material. Water has a dielectric constant of approximately 80, while that of the solid constituents of wheats and flours is approximately 10. Other electrical apparatus, such as the Tag-Heppenstall, operate on the principle of conductivity. By means of such apparatus moistures can be determined in a few seconds, but the results must be correlated with existing methods and a number of difficulties arise It is generally possible to obtain the natural moistures of wheats fairly easily, but when surface moisture enters, as in the case of conditioned wheats, the relationship is not so simple These methods have been investigated and reported upon by Coleman (Cereal Chem. 1931, 8, 315) Another system of quick moisture determination is that used by Brabender and it is claimed that this has advantages inasmuch as it will give a correct result whether the moisture is surface moisture or moisture more closely associated with the material in question This method depends on the fact that the introduction of a moist material in a circuit of high frequency has a definite "damping" effect which can be measured and which is directly related to the moisture content of the material It is claimed that the result is independent of moisture distribution, temperature, bushel weight, and fluctuations in the current.

Ash.—The determination of ash is a matter of some importance. For example, the ash of the true endosperm of wheat is probably something under 0 30%, while the ash of pure husk is

probably in the region of 8·0%. The ash of a milled product, therefore, unless there is any extraneous mineral matter present, will indicate roughly the proportion of endosperm to husk. Normally the cereal substance is burnt in a controlled muffle furnace at a temperature of approximately 600°C. until all that remains is light, fluffy mineral matter. This is then accurately and quickly weighed, as the material is hygroscopic and tends to take up moisture rapidly, and the percentage of mineral matter thus determined. Normally such ash determinations can be completed in about 2 hours. A number of suggestions have been made for shortening this time. Spalding (Cereal Chem. 1930, **7**, 93) has suggested the use of magnesium acetate in the presence of oxygen; Klopfstein (*ibid.* 189) has suggested a method of direct weighing. Walters (*ibid.* 83) has suggested the use of lanthanum nitrate in 40% alcohol, while Bowen (*ibid.* 1932, **9**, 158) has suggested the use of 1 in 19 nitric acid. Whatever method is used it is not possible to get reliable results much under an hour, although it has been proposed by Guillemet and Schell (Z. ges. Getr.-Muhlenw. 1932, **19**, 158) to use a temperature of 1,000°C. and to obtain an ash, under strictly controlled conditions, in 7 minutes. The use of glycerol-alcohol to assist ashing is also popular.

The ashing of bread requires special consideration in view of the possible loss of chloride in the operation. Probably the best results are obtained by ashing at 500°C. in the presence of a definite amount of sodium carbonate whose weight is known from a controlled determination.

Protein.—The protein determination has largely replaced the crude method of washing out the gluten and weighing it both wet and dry. Generally speaking, the protein determination is made by the Kjeldahl-Gunning method for nitrogen, a factor of 5·7 being employed for flour. For certain other cereal products, such as feeding stuffs, the usually accepted figure for multiplying the nitrogen content to obtain the protein percentage is 6·25. The digestion of the cereal with sulphuric acid and potassium sulphate prior to the distillation can usually be completed in a little over an hour. It is usual to take 1 g. of the material, 8 g. of nitrogen-free potassium sulphate, together with 20 c.c. of pure concentrated sulphuric acid and a crystal or two of copper sulphate. As the whole process may take 3 to 4 hours, numerous suggestions have been made with the idea of reducing the time. Harrel and Lanning (Cereal Chem. 1929, **6**, 72) have investigated the relation of the quantity of sodium sulphate to the time of digestion, while Watkins (*ibid.* 1930, **7**, 168) gives data and information on procedures which are helpful in saving time in doing large numbers of protein determinations. Davis (*ibid.* 518) has investigated the influence of the catalysts, copper and mercury, and of extra heat; also the effect of increasing the sulphate concentration. Lauro (Ind. Eng. Chem. 1931, **3**, 401) has suggested the use of selenium oxychloride to speed up the digestion time. By this latter method the time of digestion can be reduced from the normal $1\frac{1}{2}$ hours to 20 minutes.

Hydrogen-ion Concentration.—The importance of the determination of hydrogen-ion concentration in cereal substances has diminished of recent years, but normally the quinhydrone or glass electrode is employed. Colorimetric determinations can also be conveniently made and these will be found described in Kent-Jones and Herd, "Modern Cereal Chemistry," 1927.

Fats.—Fats are normally determined by extraction with ethyl ether or light petroleum, and difficulties in this estimation have been dealt with by Herd (Cereal Chem. 1927, **4**, 370), who advocates a preliminary drying for one hour before direct ether extraction. Herd and Amos (*ibid.* 1930, **7**, 251) conclude that direct ether extraction in the case of cooked cereal products, such as bread, does not remove all the fat, and recourse must be made to the acid hydrolysis method. Direct ether extraction gives essentially a measure of the free fats, but the acid hydrolysis method gives the total fat content, *i.e.* free fat plus the fat liberated from combination.

Diastase.—It is of great importance to millers and bakers to know to what extent a flour will tend to produce maltose when it is digested with water, as the quantity of maltose so produced seems to run approximately parallel to that produced when flour is fermenting as a dough and is, therefore, directly related to one of its principal characteristics in fermentation. The Lintner method has not proved satisfactory, as this is based on the attack on a soluble starch of the diastase extracted from the flour. What is wanted is a method in which the diastase acts on the raw starch. Fortunately, the method proposed by Rumsey (Amer. Inst. Bak. 1922, Bull. 8) has proved to be useful. In this the flour is incubated with a definite amount of water for one hour at 27°C. At the end of this period further diastatic activity is inhibited with sulphuric acid and sodium tungstate and the maltose present in the clear filtrate determined. Since its proposal this method has been investigated by a number of workers. Kent-Jones, "Modern Cereal Chemistry," 1927, p. 350, has suggested a modification suitable for routine analysis, utilising the methylene blue volumetric method of Lane and Eynon, while Malloch (Cereal Chem. 1929, **6**, 175) has indicated certain modifications which are worthy of attention. Ritter (Z. ges. Getr. wesen, 1928, **15**, 13) used Bertrand's method of sugar estimation (cuprous oxide from reduced Fehling's solution dissolved in acidified ferric sulphate and the ferrous salt so formed titrated with permanganate) to determine the maltose content after the usual hour's incubation at 27°C. More recently Blish and Sandstedt in a series of papers in Cereal Chemistry (1932 to 1934) have advocated more precision in this test. The flour is incubated at 30°C. with a definite buffer solution for one hour and the inhibition with sulphuric acid and sodium tungstate carried out as before. The determination of the maltose, however, is made by a modification of the Hagedorn-Jensen method for the estimation of sugar in blood.

Proteoclastic Enzymes.—The difficulties attending the estimation of the activity of the proteoclastic enzymes in flour are serious, but the matter has been carefully investigated by

Cairns and Bailey (Cereal Chem. 1928, 5, 79), who suggest that the Sørensen formol titration method is the most suitable. The varying proteoclastic powers of such materials as malts on doughs can probably best be determined in a comparative way by the use of their relative slackening action as registered in modern dough-testing machines.

Flour Colour.—Normally this is determined purely comparatively by use of the Pekar test. In this test a slab of flour is dipped in water and a slight darkening of the colour, related to the amount of branny specks present, occurs on drying. The test is open to a number of disturbing factors as has been pointed out by Alcock and Ediger (Cereal Chem. 1929, 6, 410). A more recent test is to add to the wet Pekar test as soon as it is made a 1% solution of pyrocatechol in methylated spirit. On standing for about 15 to 20 minutes, this solution picks out each individual bran speck present. A method for the determination of flour colour in which two independent estimations are made, one depending on the yellowness due to the carotene and the other on the dullness imparted to the flour by bran particles, etc., present, has been advocated by Kent Jones and Herd (Analyst, 1927, 52, 443) in an effort to overcome certain difficulties such as the influence of the granularity of the flour, etc., and to obtain thereby a permanent numerical record. Flour colour has been extensively investigated by Ferrari and Bailey (Cereal Chem. 1929, 6, 218, 347, 457). The comparison of crumb colours of loaves by visual estimation is rendered difficult by variation in texture. The method of Kent-Jones and Herd can, however, be successfully employed with bread.

Bacteriology.—Recent years have seen an investigation into the bacteriology of wheaten flour, particularly with respect to the bread disease known as "rope," and the original investigations of Watkins (J.S.C.I. 1906, 25, 350) have been extended. For a study of the general bacteriology of wheaten flour, attention is directed to the paper of Kent Jones and Amos (Analyst, 1930, 55, 248) and in the case of rope to that of Amos and Kent Jones (*ibid.* 1931, 56, 572). These investigators have pointed out the widespread nature of *Bacillus mesentericus* and have given a method for its determination. They have also indicated the fermentation and baking conditions under which it may best be suppressed. A useful apparatus for testing for "ropiness" in bread has been designed by Bunzell and Forbes (Cereal Chem. 1930, 7, 465) and Bunzell and Kenyon have recently extended the work in a further paper (*ibid.* 1932, 9, 161). Their method depends on the splitting up of hydrogen peroxide by the enzyme catalase present in the bacteria.

Moulds grow easily on bread and trouble from this source is occasionally encountered. Most mould spores are, of course, killed at oven temperature, so that generally the contamination comes after baking. The principal moulds are:

Penicillium glaucum (greenish-blue).
Mucor mucedo (white).
Aspergillus niger (black).

A paper on the "Non-survival of Red Mould of the *Monilia Sitophila* Group at Baking Temperature" was given by Morison (Cereal Chem. 1933, 10, 462).

Gluten.—When wheaten flour is made into a dough and then washed cautiously underneath a stream of running water, it is possible to wash away the starch and leave behind an elastic brownish residue which consists principally of protein. This is known as gluten. Wheat is the only cereal which acts in this way and it is due to the presence of gluten that wheat flour forms its characteristic dough. In consequence of its importance, this peculiar substance has been investigated by a large number of scientists. Various flours have quite different baking properties and so an intensive study into the nature of their glutens has been carried out, first from a purely chemical point of view and later and more successfully from a colloidal aspect. It should, however, be remembered that gluten is merely something which is left behind after a particular operation, namely, washing, and it is not a pure substance. Although it consists principally of protein, it also contains some starch, fibre, sugar, etc., which have not been removed in the washing operation. Furthermore, it does not contain all the proteins of the flour, some of which are soluble and pass away with the starch in the washing water. The main ingredients, however, of gluten are the two well known proteins—*gliadin* and *glutenin*. At one time the proportion of gliadin to glutenin was thought to be of importance in determining the nature of the gluten and hence of the baking quality of the flour, but the early methods for the determination of these two proteins were open to criticism. Both these proteins have been extensively studied in recent years. Blish (Cereal Chem. 1930, 7, 421) concludes after a careful survey of the literature, particularly recent American work, that trustworthy and dependable methods for the identification and quantitative separation of the individual flour proteins, other than gliadin, are not available. Glutenin is so apt to be changed in the extraction methods employed that the results are valueless. Generally speaking, the American investigators are of the opinion that the ratio of glutenin to gliadin varies only slightly between different sorts of wheat. Many European chemists, however, are still of the original opinion of Fleurent, who thought that in a gluten associated with good baking quality there was a definite ratio between the glutenin and gliadin. Berliner (Z. ges. Getr.-Muhlenw. 1927, 64) is of the opinion that the determining factors in gluten quality are, first, the proportion of gliadin to glutenin, and, secondly, the dispersion degree of glutenin. Undoubtedly the colloidal nature of the gliadin glutenin complex has a profound effect on the "strength" of the flour.

The function of the two principal proteins, glutenin and gliadin, in the chemistry of bread-making has already been discussed (p. 75). Gluten is a colloidal material and its properties undoubtedly depend upon the electric charges it holds which, in turn, depend upon the electrolytes present. These points of view are

clearly put forward by Bungenberg de Jong (J.S.C.I. 1933, **52**, 291T).

At one time cereal chemists paid a great deal of attention to the relative proportions of wet and dry gluten obtained from flour, but this determination has to a large extent been superseded. A useful survey of the early work on gluten and of methods for its quantitative estimation in various flours is to be found in Jago's "*Technology of Breadmaking*," 1911. The modern dough testing machines are essentially machines for determining the physical properties of the glutens in various doughs. They have proved more useful than the earlier methods based on the examination of the nature of the extracted gluten as the behaviour of the gluten depended largely on the method of extraction employed.

Gliadin.—Gliadin is one of the principal protein ingredients of flour. It is extracted from gluten by treatment with 70% alcohol and is a soft, sticky material. It is generally stated that, while glutenin gives solidity to the gluten, it is the gliadin that does the binding; the gliadin sticks to the glutenin and so prevents it being washed away in the process of extraction of the gluten by washing. Osborne and Voorhees (Amer. Chem. J. 1893, **15**. 392) have given the elementary analysis of gliadin as :

	%
Carbon	52·72
Hydrogen	6·86
Nitrogen	17·66
Sulphur	1·14
Oxygen	21·62

A material which is apparently identical with wheat gliadin can be extracted from rye with 70% alcohol, although rye is not capable of forming a gluten. Osborne and Clapp (Amer. J. Physiol. 1906, **17**, 231) give the products of the hydrolysis of gliadin as follows :

	%
Glycine	absent.
Alanine	2·00
Valine	0·21
Leucine	5·61
Proline	7·06
Phenylalanine	2·35
Aspartic acid	0·58
Glutamic acid	37·33
Serine	0·13
Tyrosine	1·20
Cystine	0·45
Lysine	absent.
Histidine	0·61
Arginine	3·16
Ammonia	5·11
Tryptophan	present.
Total	65·80

It will be observed that there is no glycine or lysine but that the proportion of glutamic acid is very high.

Glutenin.—The other protein in flour which, together with gliadin, forms the major portion of gluten, is known as glutenin. It is insoluble in water and alcohol but can be extracted from dough with dilute alkali. According to Osborne and Voorhees glutenin has the composition :

	%
Carbon	52·34
Hydrogen	6·83
Nitrogen	17·49
Sulphur	1·08
Oxygen	22·26

According to Osborne and Clapp (Amer. J. Physiol. 1906, **17**, 231) the products of hydrolysis are :

	%
Glycine	0·89
Alanine	4·65
Valine	0·24
Leucine	5·95
Proline	4·23
Phenylalanine	1·97
Aspartic acid	0·91
Glutamic acid	23·42
Serine	0·74
Tyrosine	4·25
Cystine	0·02
Histidine	1·76
Arginine	4·72
Lysine	1·92
Ammonia	4·01
Tryptophan	present.
Total	59·68

Glutenin is known as a glutelin. Woodman (J. Agr. Sci. 1922, **12**, 231) suggested that the glutenin from strong flour was chemically different from the glutenin from weak flour, although by ordinary methods of analysis they were indistinguishable. To investigate the matter he employed a racemisation method and concluded that strong wheat synthesised one type of glutenin and weak wheat a different type. Blish and Pinckney (Cereal Chem. 1924. **1**, 309) re-investigated this point and concluded that it is highly improbable that variation in the respective flour strengths of wheats is due to difference in the configurations of their glutenin molecules, and this view is generally accepted at the present time. D. W. K.-J.

BREAD FRUIT. The fruit of *Artocarpus incisa.* The trees grow freely in certain tropical islands and yield an abundance of nearly spherical fruit weighing up to 5 or 6 lb. The central portion consists largely of starch of which a considerable amount is converted into sugar. A larger variety, *A. integrifolia*, yields fruit weighing up to 25 lb. which contains seeds said to resemble chestnuts in composition and flavour.

The fruits are usually collected green and cooked, or the pulp is removed and dried to yield a flour having the composition :

Water.	Protein.	Fat.	Starch.	Fibre.	Ash.
14·3	1·0	0·2	83·8	0·2	0·4

Pairault (Bull. Assoc. Chim. Sucr. 1900–1901,

No. 1, 77) gives the composition of whole fruit from the Antilles as:

Water.	Protein.	Fat.	N free ext.	Fibre.	Ash.
46 2	2 34	0 4	45·1	4·2	1·8

The edible portions of two Hawaiian varieties are shown by Thompson (Hawaii Agric. Exp. Sta. Rept. 1914, 62) to contain: total solids 41·8, 26·9, protein 1 58, 1·58, fat 0 19, 0 52, N-free ext. 37·9, 22 7, acids 0·07, 0 11, reducing sugars 1·75, 4 93, sucrose 7·7, 9 7, fibre 1·2, 1 0, ash 0 9, 1·1. A. G. Po

BREEZES. (*Braise*, Fr.) The dust of coke or charcoal The coke burner applies this term to the small residual coke obtained in coke burning The sifted ashes removed from houses is called " breeze," and sold under that name to brickmakers and others. An arrangement for burning breeze is described in J S.C I 1881, 5, 425.

BREITHAUPTITE v. ANTIMONY.

BREMEN BLUE and **LIME BLUE** are essentially copper hydroxide, $Cu(OH)_2$, associated with copper carbonate and calcium carbonate respectively, formerly used as pigments

BREWING. The raw materials employed in brewing are water, malt and hops. Ungerminated or raw grain, prepared grain and sugar are often used as adjuncts supplying a portion of the extract, the malt supplying the major portion.

Water.—Water as used for brewing must be free from metallic contamination or substances which may interfere with the quality of the beer as regards taste and appearance Whilst it must be free from organic pollution, the process of brewing includes adequate sterilisation so that the standard of purity actually necessary in the water is not so high as in the case of water for public supplies.

If the water supply is soft it must be artificially hardened. Normally brewers use well waters which are naturally hard. The types used are illustrated by the following table, which includes some well-known waters used for brewing pale and dark beers. It will be seen that soft water is used for Pilsener beer.

	Parts per 100,000			
	Burton.	Dublin	Pilsen	Munich
$Ca^{\cdot}$	15–30	10	1–3	11–27
$Mg^{\cdot}$	3–9	0 5	1–2	3–12
$Na^{\cdot}+K^{\cdot}$	4	1	0 5	—
SO'_4	50–100	1–5	1–4	0–12
Cl'	4	2	0 5	0–13
CO'_3	20	14	—	23–47
NO'_3	2–10	—	—	—

In general terms it may be stated that the desirable constituent is either calcium sulphate or chloride, present in quantity equivalent to 10–30 parts per 100,000. Much smaller quantities of magnesium, sodium and potassium may be present. Carbonates in excess of 1–2 parts of CO'_3 per 100,000 are undesirable. Of nitrates, the less present the better, as they have been found to weaken the yeast, and thereby indirectly affect the beer. Iron is undesirable as it may have an adverse influence on colour and flavour. The choice between sulphates and chlorides is largely one of type of beer, the Burton type requiring the former, fuller drinking types the latter. The total chloride content including sodium chloride and expressed as such may be as high as 50 parts per 100,000 when mild ale is to be brewed. The actions of calcium salts may be represented, not accurately but in their general effects, by the following equations (W. Windisch, Woch. Brau. 1913, 30, 514).

$$3CaSO_4+4K_2HPO_4 = Ca_3(PO_4)_2+3K_2SO_4+2KH_2PO_4$$

$$3CaCO_3+4KH_2PO_4 = Ca_3(PO_4)_2+2K_2HPO_4+3H_2O+3CO_2$$

Malt, on mashing with water, liberates inorganic phosphates and, the reaction being about p_H 5 5, these will comprise both KH_2PO_4 and K_2HPO_4. Thus calcium sulphate or chloride will have the effect of acidifying the mash, which is desirable within reasonable limits, whereas all carbonates will have the reverse effect. Magnesium salts react in a similar manner, but less effectively. Owing to the solubility of secondary magnesium phosphate, $MgHPO_4$, the reaction does not go to completion Although Southby recommended a proportion of calcium to magnesium of 3 . 1, and many authorities still hold by this, there is an increasing tendency to reduce the proportion of magnesium used in hardening brewing water for mashing purposes. There is apparently enough magnesium normally present in malt to supply the requirements of yeast nutrition. On the other hand, it is considered to contribute undesirably to the flavour and clarification of the beer. The beneficial effect of the salts in the water, to which must be added those of the malt and hops, include not only yeast requirements but also any assistance they may give in influencing the properties of the wort proteins. Globulins, present in malt, are more readily soluble in the presence of salts, and coagulable proteins which are removed by boiling are assisted in their coagulation which must be as complete as possible. In this latter respect, calcium and sulphate ions, being divalent, presumably function more effectively than sodium and chlorine ions.

The main influence of the water salts, however, is on the reaction of the wort, which is most important. Bicarbonates in the mashing liquor have the effect of making the reaction more alkaline, as much as 0 3–0 4 unit of p_H, whereas other salts of calcium, and, to a much less degree, magnesium, have the opposite effect. These effects persist in diminishing degree throughout the process of brewing and are reflected in the reaction of the final product. The desirable values of p_H at the respective stages of brewing will be dealt with later.

Where the natural water available to the brewer does not conform to requirements, it is usual to adjust it by suitable means. Of the objectionable constituents, nitrates cannot be removed, only dilution with nitrate-free water is possible. Iron is usually derived from the

Green Sands adjoining chalk formations and, occurring as ferrous bicarbonate, is deposited along with calcium carbonate on boiling. Calcium carbonate may be removed by boiling, by lime treatment, or by neutralisation with sulphuric or hydrochloric acid according as sulphates or chlorides are desired for effect on flavour. Lactic acid has also been used, and this treatment corresponds, at least in some part, to what is sometimes practised in lager brewing and yeast manufacture, viz., the inoculation of the mash, or of a part of it, with lactic acid-forming bacteria. The latter process, however, also promotes a certain amount of peptonisation of the malt proteins, and so goes further than merely changing the p_H of the mash. If an adequate quantity of other salts of calcium is already present in the natural water, the carbonate should preferably be removed by a process other than neutralisation. Of these treatment with slaked lime is sometimes preferred, the process being usually carried out in two stages. The first involves the addition of the necessary quantity of slaked lime, but the mixture arrives at an equilibrium with excess of both calcium hydroxide and bicarbonate present in solution. It is best to heat the liquor by steam coils to the temperature required for mashing during the progress of this reaction. Excess of lime is then neutralised by an appropriate quantity of acid sodium or potassium sulphate (J. H. Collett, J. Inst. Brew. 1931, **37**, 274). This process has the advantage of removing also iron and carbonates other than calcium. The removal of the latter can also be effected by neutralisation with acids, the quantity added being calculated after previous determination of the total alkalinity of the water. An arrangement for controlling the rate of addition of acid has been suggested by D. McCandlish and G. Hagues (J. Inst. Brew. 1929, **35**, 61). After, or concurrently with, the removal of objectionable constituents from the water, any addition of desirable ones is made, usually gypsum or a syrup of calcium chloride or both, together possibly with magnesium salts or sodium chloride. In general the stronger the beer the larger the quantity of salts desirable.

Whilst the foregoing remarks apply to the brewing of most types of beer, it is not uncommon for soft water to be used in the brewing of stout, and in some cases, of lager beer. It is hard to find theoretical justification for the practice, even although empirical grounds (flavour) may exist.

Malting.—Malt is made from barley, occasionally from wheat or oats. Types of barley, both British and foreign, used in making malt for brewing purposes are dealt with in the article on barley. The grain is steeped in water, allowed to germinate until a certain degree of growth, accompanied by softening and " modification " of the corns, has been attained. The process is stopped by drying, and the malt cured by heat until the desired depth of colour and biscuity flavour have been attained.

Germination, morphologically, leads to a growth of the embryo up the dorsal side of the corn beneath the outer protective layers, accompanied by the development of a number of rootlets. The whole corn softens and the contents become crumbly. Respiration is proceeding and loss of solid matter is involved. Histologically the cell walls of the endosperm as viewed microscopically progressively disappear; first, those in the neighbourhood of the embryo and aleurone cells, later those of the interior. They are made to re-appear by suitable staining, *e.g.* with Congo red (J. Grüss, Woch. Brau. 1896, **13**, 729; A. R. Ling, Brewers' J. 1904, **40**, 741). Some of the starch granules in the vicinity of the embryo exhibit signs of erosion. In Fig. 1 the advancing disintegration of the contents of the grain is indicated by shading. A is at 3, B at 6, and C at 10 days. D is a transverse section of B at *ab* (Brown and Morris, J.C.S. 1890, **77**, 470).

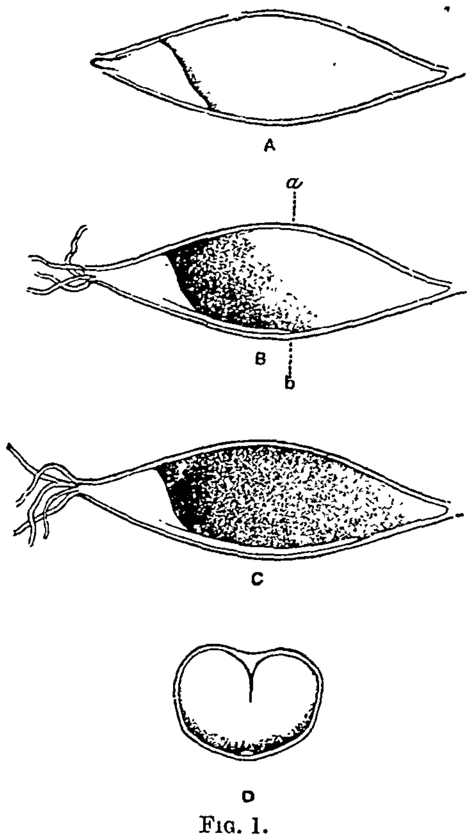


FIG. 1.

Biochemically considerable changes are taking place. An enzyme, usually termed *cytase*, is responsible for the degradation of certain hemicelluloses, which are partly structural and partly function as food reserve. These include hexosans which break down ultimately to hexoses, and pentosans which similarly yield pentoses. Of pentosans there are 8–12% in the corn, and, whereas only 3% of this quantity is soluble in the barley, from 11–12% of the total malt pentosans are soluble (H. Fink, Woch. Brau. 1935, **52**, 265; J. L. Baker and H. F. E. Hulton, J.C.S. 1917, **111**, 121; H. Lüers, Woch. Brau. 1935, **52**, 249). Lichenin also is degraded by cytase (or lichenase), which apparently is a composite enzyme, the ultimate

products being cellobiose and glucose. The *formation of cytase*, which is present in small quantity after steeping, continues until the grain is ready to go on the kiln (H. Lüers and L. Malsch, Woch Brau 1929, **46**, 163). The effect *of the cytase activity during germination* is to render the cell walls of the endosperm more permeable to enzymes and their hydrolytic products From the maltster's point of view it is *to render the malt tender and friable*

A most important biochemical feature of germination is the change in the diastase. The active amylase of resting barley is a β amylase in the sense of Kuhn that is to say, it produces maltose in the β-form, which mutarotates to the stable equilibrium of α- and β forms Under normal conditions, maltose equivalent to two thirds of the starch is formed, the remainder of the conversion products being Baker's α-amylodextrin There is a further store of amylase in resting barley which can be extracted if such a protease as papain is added to the extracting medium (J S Ford and J M Guthrie, J Inst Brew 1908, **14**, 61) This also appears to be *amylase of the β type, but according to* E. Waldschmidt Leitz, M Reichel and A. Purr (Naturwiss 1932, **20**, 254) an inactive form of α amylase is also present in barley, and this *becomes active in the presence of the activator*, termed by these authors amylokinase, which is present in malt. Other authors, H Luers and W. Rummler (Woch. Brau 1935, **52**, 9), have failed to confirm the existence of amylokinase in germinated barley Malt contains both α- and β amylases in the active form, but the β enzyme is in excess (E. Ohlsson, Z physiol Chem. 1930, **189**, 17) The α or dextrinising amylase of malt can be conveniently measured by its action on α-amylodextrin. L Fletcher and J. Westwood (J Inst. Brew 1931, **37**, 470) have worked out a method based on this principle The same authors (*ibid* 1930, **36**, 550) have also described a method for the *determination of the liquefying power of malt* amylase based on viscosity measurements It is not yet clear whether or not the two actions are due to the same enzyme. The characteristic *feature of α-amylase*, apart from the mutarotation behaviour of its fission products, is the comparatively early stage in the starch degradation promoted by it, at which the hydrolytic products cease to give an iodine reaction. Methods of determination based on this principle made concurrently with measurements of liquefying and saccharifying activities have led to the conclusion that liquefaction and dextrinisation of starch are not both dependent solely on the quantity of α amylase present (H. Luers and W. Rummler, *l c.*). These *activities first* manifest themselves, in anything more than traces, on the second or third day of germination, whereupon they increase rapidly until about the *fifth or sixth day, and then remain almost* unchanged until kilning reduces them by more than half. Throughout the period of increasing values a greater quantity is extracted by water *containing* papain than by water alone, and this is true also of the saccharifying enzyme (H. Lüers, Woch. Brau. 1935, **52**, 249). During malting, whilst much change occurs in the quantity and character of the diastase present, comparatively little diastatic transformation takes place. Of the dry matter originally present, about 12% is transformed, about 4% passing on by anabolic processes into rootlet and embryo tissue and 8% remaining as sugars in the malt, most of the latter occurring as cane sugar, the rest as reducing sugars other than maltose, which is absent. A further quantity, *about 7%, is consumed in respiration*. The maltose produced by diastatic enzyme is hydrolysed to glucose by a maltase which is formed mainly or wholly during germination. The properties *of this maltase*, apart from its power of splitting maltose, do not appear to be identical with the better known maltase of yeasts. How the glucose, so formed, is transformed into cane sugar is unknown.

The proteolytic enzymes of malt appear only during germination. They include (1) a proteinase, which attacks proteins and peptones, degrading them to simple peptides, and (2) at least two dipeptidases. The proteinase acts optimally at reactions approximating to that of the isolectric point of the substrate protein, or as near to it as solubility permits. This is probably, in the case of barley proteins, at the reaction of the germinating barley, which *changes from about p_H 5·2 to p_H 6·0 as germination* proceeds. The dipeptidases split alanylglycine and leucylglycine at the optimal p_H 7 8 and 8 6 respectively. The peptidase activity increases steadily throughout germination, but is largely or wholly destroyed on the kiln, according to the curing conditions (K. Linderstrom-Lang and M. Sato, Compt. rend. Trav. Lab. Carlsberg, 1929, No. 17; M. Sato, *ibid.* 1931, No. 1; H. Luers and L. Malsch, Woch. Brau. 1929, **46**, 265, 275; R. H. Hopkins and J. A. Burns, J. Inst. Brew. 1930, **36**, 9; R. H. Hopkins and H. E. Kelly, Biochem. J. 1931, **25**, 256; H Luers, Woch. Brau. 1935, **52**, 249). The soluble nitrogen content of the corn increases to *about twice its original value during the early* days of germination; thereafter, although the proteinase is still functioning, resynthesis in embryo and rootlets roughly balances degradation. A considerable transport of nitrogen from endosperm to embryo takes place. Whereas about 86% of the original barley nitrogen was present in the endosperm, only 50% of the malt nitrogen is there, about 40% of the former having been degraded sufficiently to have passed across into the embryo. Probably more than 40% has been attacked in less degree. 10–25% of the total barley nitrogen and 25–30% of the malt nitrogen are soluble in cold water. The content of "formol" nitrogen also *undergoes a marked increase during malting.*

The nitrogen content of barley varies between 1·2 and 2·4% of the dry weight, although such barleys as contain about 2% would rarely be used for making brewers' malt. The character and quantitative relationships of the proteins are dealt with in the article on barley. During malting the hordein and glutelin are degraded by the proteinase which is secreted or activated from a zymogen, to yield chiefly non protein nitrogen (proteoses and peptones). The decrease in quantity of glutelin, *e g.* from 0 245 to 0 160 g

as nitrogen per 1,000 corns, is not so marked as that of hordein, *e.g.* from 0·206 to 0·075 g. (same barley), and ceases sooner. Indeed, there appears to be a resynthesis of glutelin in the embryo as indicated by an increase in this fraction after about the tenth to twelfth day of germination (L. R. Bishop, J. Inst. Brew. 1929, **35**, 323).

The activity of phosphatases, very slight in ungerminated barley, increases throughout germination but falls to about half its maximum value during kilning. The effect of this enzyme or group of enzymes is to liberate inorganic phosphates from various organic compounds containing phosphorus, proteins, carbohydrates, phytin, etc., about 15–30% of the phosphorus being so liberated.

Other enzymes functioning include catalase, which increases and falls much as the phosphatase activity, and lipase, which appears to be activated from a protein-lipase complex preformed in the barley. Sulphur, set free from sulphur-containing proteins, ultimately forms inorganic sulphates.

The buffer substances derived from malt exercise so important a function in brewing that note must be made of their formation in malting. The cold water soluble buffer substances of barley are reduced to about half by steeping, but this reduced quantity is increased to two or three times as much during the third to sixth day, after which very little change occurs either during subsequent germination or kilning. Concurrently with increase in buffers, the p_H of the aqueous barley extracts rises from about 5·2 to 6·0, falling a little during curing to about 5·8 (R. H. Hopkins and H. E. Kelly, J. Inst. Brew. 1929, **35**, 408).

The selection of barley is usually based on inspection of such characters as uniformity of shape and size, colour, odour, dryness, apparent thinness of skin, whiteness of endosperm (a number of corns being cut through in a cutter). Analytical valuation, which nowadays can be performed in one or two hours, includes determination of percentage moisture, total nitrogen and thousand corn weight, the latter two results being always expressed on the moisture-free basis. To some extent these factors have been taken into account in the subjective (hand) valuation. Another important laboratory determination is the percentage of corns that will germinate. In Germany systems are in use whereby a certain number of marks are awarded out of a maximum available for each of the above features, the highest maxima being awarded for uniformity in size, thousand corn weight, and nitrogen content. As regards the last feature, from 1·45 to 1·68% nitrogen secures full marks. Valuation by hand examination by experts in Great Britain has in recent years placed barleys into grades, the mean nitrogen contents of which have been found to rise with fall in grade, the highest grade often yielding as low a nitrogen percentage as 1·2–1·3. Quantitatively, the value of the barley in terms of potential extract can be calculated, if the variety is known, by means of the following formula, deduced by L. R. Bishop from observations and records of barleys and malts made from them, the figures being treated statistically. The formula applied to Plumage-Archer barley is as follows:

$$E=108{\cdot}3-10{\cdot}5N+0{\cdot}20G,$$

where E=extract of the moisture-free malt in lb. per quarter, N=nitrogen content on dry barley as percentage, and G=the weight of 1,000 dry corns in g. (L. R. Bishop and F. E. Day, J. Inst. Brew. 1933, **39**, 545). For barleys other than Plumage-Archer and Spratt-Archer the constant 108·3 may have to be altered to 108–110 for two-rowed and 102–103 for most six-rowed barleys. In certain maltings, the malting loss may be above or below that of the standard malting on which the formula was worked out, so that the constant 108·3 can be appropriately adjusted. This possibility must be kept in mind (L. R. Bishop, J. Inst. Brew. 1930, **36**, 421).

Alternatively, if the percentage of germinating corns is known, the potential extract can be calculated in terms of the barley, by means of the formula:

$$R=[132-15N+0{\cdot}2G(+1-0{\cdot}3X)]\times\frac{DM}{100},$$

where R=extract on the raw barley,

$$\left.\begin{array}{l}N=\%\text{ nitrogen}\\ G=\text{weight in g. of 1,000 corns}\end{array}\right\}\text{of moisture-free barley,}$$

X=% dead corns,

and DM=% dry matter.

The value, 132, applies to English barley generally, 126 would apply to Californian, 128 to Indian barley, etc. (L. R. Bishop, J. Inst. Brew. 1936, **42**, 105).

Unless barley has been harvested under the best climatic conditions, its germination is markedly improved by kiln drying, either on an ordinary kiln or in a drying drum at a temperature between 38°–50°C. (100°–120°F.). The wetter the barley, or the feebler its germinative vitality, the lower the drying temperature should be. Drying should be followed by about two months' storage. Storage within these limits improves a barley, whereas a barley containing 16% or more of water would deteriorate on storage. Before malting the barley is screened.

Steeping takes place in either rectangular cisterns made of blue brick or cement, or better, in conical ones made of iron. In either case a false bottom permits the withdrawal of water. Steeping occupies from 48–70 hours according to the type and condition of the grain, the temperature being 10°–13°C. (50°–55°F.). The higher temperature shortens the time required for steeping and accelerates germination, the lower temperature delays matters, but, except for this, is not harmful. Excessive steeping impairs vitality, deficient steeping may accelerate the start of germination, but sprinkling must be resorted to subsequently. Good English and Californian barleys require less, hard and dry barleys, *e.g.* Chilean and Australian, more steeping time. It is important that the steeped barley be removed at the proper stage of steep ripeness. Previous washing of the grain, frequent changes of steep water, and intermittent aeration are usually carried out. Some maltsters

include a little lime water in the first lot of steeping liquor, but the advantage is doubtful A little matter, about 1%, is extracted from the corns, almost entirely from the husk. One layer within the husk is semi permeable, so that salts present in the steep water do not penetrate the grain, except in the case of damaged corns (A. J Brown, Proc Roy Soc. 1909 (B), **81**, 82) The steeped barley is dropped from the cistern on to a growing floor constructed as uniformly flat as possible with tiles or cement. To give germination a start the grain is at first often heaped up in a deeper layer than it will subsequently form, known as a couch Respiration generates heat, which escapes as rapidly as generated only if the germinating grain is spread out in a layer a few inches deep To raise the temperature it is heaped up, to lower it it is thinned out The couch is broken down after a few hours, the temperature being now about 13° (55°F), between which temperature and 15 5° (60°F) (or higher abroad) the grain is usually confined during the whole of germination Turning by suitable tools, to keep the moisture and temperature uniform and to enable carbon dioxide to escape freely, is performed at intervals Temperature may be raised, if necessary, by sprinkling with water, after some has evaporated, thereby increasing respiration, but this means loss of carbohydrate matter and loss of extract Too much aeration encourages excessive respiration, whereas too little weakens germination (H. Schjerning, Compt rend Trav. Lab. Carlsberg, 1910, **8**, 169; H T. Brown, J. Inst. Brew. 1907, **13**, 394, 1909, **15**, 170).

The grain as it leaves the steep usually contains about 42–45% water; this is sometimes much reduced before it goes on to the kiln. If no sprinkling has been practised, the green malt will need little special attention, but if still rather wet, it must be "withered" or dried in air currents till the moisture content is down to 40% or thereabouts, or even less.

In this mechanical age it is surprising that machinery is not more often employed. However, much in malting and brewing is in the nature of an art rather than a science. Pneumatic malting in rotating drums, in which everything is under control, is practised by some maltsters Saturated or dry air as required, filtered from dust, thus eliminating mould, and at any temperature desired, is made to pass through the barley from the outer to the central channel of the drum. Excessive respiration losses are encountered in this method, but it has certain advantages. On the Continent germination is sometimes performed in deep layers of three to four feet, on perforated floors with air sucked through, and turning is effected by powerful mechanical turners (Saladin system) Continental maltsters often leave the malt less completely modified than is usual in this country, less loss by respiration is involved, any loss of extract which would normally result from under-modification is avoided by the scientifically planned decoction-system of mashing employed. The withered malt is now dried on a kiln Kilns may have one, two or three drying floors made of perforated tiles, iron plates, or wire mesh, and situated one above the other and surmounted by a conical or pyramid-shaped roof with a cowl or, better, a fan to assist draught. Single-floor kilns are usual in Great Britain; three-floor are rarely found here, but sometimes on the Continent. The latter are more economical in fuel consumption but more difficult to manage. Beneath the lowest floor is a suitably shaped iron disperser to distribute the heat from the fire as uniformly as possible over the kiln floor surface. This may be assisted by pipes conveying hot gases passing under the floor, or portions of it. The fire draught is automatically regulated, so that if the temperature on the floor rises too high the draught is cut down. The actual flue gases pass through the drying malt, so that care must be exercised in selecting fuel (coal or coke) which is free from arsenic On the Continent the malt is heated by air which is passed upwards through a screen of pipes inside which the flue gases are passing. The temperature of the green malt is slowly raised to about 65° (150°F.) by the end of two or three days with considerable draught passing through It must not be held too long at such a temperature as 33°–40° (90°–104°F.), otherwise enzyme action may continue. At this stage (after three days) it should be "hand dry" and contain about 6% of moisture. If a two-floor kiln is used it is dropped from the upper to the lower floor for curing. The temperature is now raised, with less and less draught, to the final curing temperature desired and maintained there for six to eight hours. Pale malts are cured at 88°–91° (190°–195°F.), mild ale malts a *little higher, and dark malts at 96°–102°* (205°–215°F.). The moisture content is now less than 2%, the malt has a biscuity flavour, the enzymes are destroyed or reduced in activity, and the rootlets are withered, reddish-brown in colour, and largely detached from the corns With the minimum of exposure to the air, for malt is very hygroscopic and must not be allowed to get slack even to 4% of moisture, the malt is conveyed to the storage bins, which must be kept airtight. Sometimes it is screened, to free it from withered rootlets or culms, before it is stored, sometimes afterwards, just before brewing.

In the "Winkler" system of kilning, occasionally practised, the green malt is loaded at a great depth, three feet or more, and hot flue gases are blown through by means of a powerful blower Drying is effected very rapidly, the malt being rushed past the danger zone in which high temperature and moisture coincide so quickly that little harm is done. Further, the very rapid evaporation set up reduces the actual temperature of the malt itself much below that of the gases passing through.

The extract yielded by malt, expressed as pounds per quarter (of 336 lb.) (*see* analysis), should be about 100 for a good home barley, and 94 for a good six-row Mediterranean type (*e g* Californian), these figures assuming the moisture to be not more than 2%. Lower figures suggest poor quality barley (small corns, high nitrogen content) or under modification. The latter is sometimes indicated by a large increase of extract, determined analytically, when the malt

is ground very finely as compared with standard grinding. Continental brewers express extract in dry solids as a percentage of the malt ("Plato" scale), the results being very nearly 0·80 of the corresponding British result. The diastatic power, in degrees Lintner, should be very roughly 20, 30 or 40 ; the colour or tint, in Lovibond degrees, should be 10, 7, and 4 respectively, corresponding to dark, mild ale and pale malts. The Lintner value should be considered only in conjunction with the colour. High nitrogen is normally accompanied by relatively high diastatic power. The percentage of solids soluble in cold water should be about 18–21 for home malts, and one or two units lower for, *e.g.* Californian. The quantity of permanently soluble nitrogen in the 10% wort prepared for extract determination, expressed as a percentage of the total malt nitrogen, is a useful result, both as an index of (protein) modification and of yeast feeding properties of the malt.

No wholly satisfactory criterion of the degree of modification of malt is yet available, although many have been suggested. This is because the various enzymes functioning during germination may not do so at the same relative rates in different barleys and under different conditions of malting. The respective stages of protein degradation, of starch degradation, changes in the character and quality of water soluble diastase, formation of other enzymes, cell wall dissolution, production of soluble pentosans, all these processes may vary in rate relatively to one another. Most of the changes have attained approximately their maximum by the fifth or sixth day of germination. After this, re-synthesis approximately balances degradation, so that most of the proposed methods of measuring modification give approximately constant results after the fifth or sixth day. Modification, as required in malt for infusion brewing purposes, is far from complete in six days.

Coloured Malts.—For brown ales, stout, and porter a proportion of darker malts, about 10%, is used in the grist. Amber malt is made by keeping the green malt wet until a high kiln temperature is attained. The diastatic power of such is low, about 10–15 degrees Lintner, and the colour high. Crystal and roasted malts are usually obtained by heating to high temperatures in rotating drums in a manner analogous to the roasting of coffee beans. In the case of crystal malt, it should be sprinkled with sugar solution before roasting.

Malt Adjuncts.—These include: (1) maize grits and other forms of raw grain, which have to be gelatinised in a converter heated by steam with the aid of a little malt grist before running into the mash tun, (2) flaked maize or rice which has virtually been treated in the above manner and dried and may be mixed with the grist before mashing, (3) invert sugar, glucose (occasionally raw cane sugar, refined cane or beet sugar), which is usually added to the contents of the brewer's copper. Sugars assist clarification of beer, and in general yield a sweeter product, which is what is in demand in certain areas. Both types of malt adjuncts, grain and sugars result in dilution of the nitrogenous matters present in the extract derived from malt, and this, if carried too far, and in low gravity beers particularly, may lead to insufficiency of nitrogenous yeast nutrients, and lack of fullness of flavour and other properties associated with proteins and peptones.

Hops give flavour to beer and contribute antiseptic matters, which is one of the reasons why beer is so free from pathogenic organisms. The hop, *Humulus*, is a diœcious plant, and the part used by the brewer, the hop cone, is the inflorescence of the female (Fig. 2).

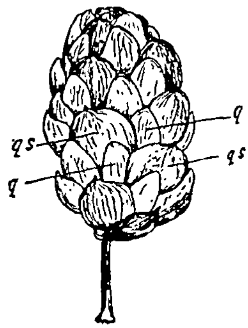


FIG. 2.

sb "stipularbract" *b* "bracteole"

(*From Percival's "Agricultural Botany,"* 1900, *p.* 325, *Duckworth & Co.*)

Normally the flowers in English and American hops become fertilised, and in such seeded hops a much greater yield per plant and per acre is thereby secured. In Central Europe fertilisation is prevented by exclusion of male plants from hop-growing areas, and a smaller cone is obtained, but of excellent quality in regard to aroma and preservative value. American hops in general have the highest preservative value of all, but many varieties possess an aroma resembling that of the black currant leaf, which causes most British brewers to use such hops either sparingly or not at all.

The chemical composition of hops is as follows :—

	% of dry matter.
Mineral matter	5–9
Protein matters	12–24
Resins	11–20
Tannins	2–6
Essential oil	0·4–0·8

together with cellulose, pentosans, pectins, colouring matter, and organic acids. The mineral portion includes potassium, calcium and lesser quantity of magnesium combined as phosphate, silicate and sulphate. Of the nitrogenous matter, the quantity which dissolves and is permanently soluble in practice approximates to the small quantity of malt proteins coagulated by boiling. It appears to be mainly assimilable by the yeast.

The tannins (H. Bilgram, Woch. Brau. 1931, 48, 493), which include *phlobaphen*, function as very weak acids, more readily soluble the more alkaline the reaction of the boiling wort. They function to some extent by precipitating pro-

teins, but it is not clear how far this takes place during boiling and how far tannin protein bodies cause objectionable hazes and turbidities later in the process. The organic acids of the hops are to some extent extracted and, either by precipitation as calcium salts, or otherwise, *function to increase the acidity of the wort*

The essential oil contains the aliphatic hydro carbon *myrcene*, $C_{10}H_{16}$, b p. 166°–168°, a sesquiterpene *humulene*, b p 263°–266° and much smaller quantities of other bodies (A C. Chapman, J C S 1895, 67, 783 , 1903, 83, 505 ; *1928, 1303) So far as hops used in the copper* are concerned the oil is largely volatilised in the steam and lost, but a little flavouring and aroma may be imparted by the hops added to the beer in cask

The most important constituents of hops are the antiseptic resins. *Humulon*, $C_{21}H_{30}O_5$, an unsaturated crystalline compound (Wollmer, Ber 1916, 49, 780 , Wieland, Ber 1925, 58, [B], 102, 2012), resinifies easily to produce the α resin. *Lupulon*, $C_{26}H_{38}O_4$, yields similarly the β resin On analysis of hops (*see* analysis) the lead salt fraction contains both humulon and a little α resin presumably derived from it, the whole constituting the α fraction, the anti septic power of which, under the standard conditions of measurement, is approximately *three times that of the β fraction. The latter* contains lupulon, resins derived from it and from humulon, and a certain amount of neutral material apparently originating from neither humulon nor lupulon All of the α and β-fractions change in time into the useless γ-fraction (T. K Walker, J Inst Brew 1925, 31, 576, F. L Pyman, J Inst Brew 1927, 33, 295) Provisionally, the antiseptic potency of hops is expressed by the formula $10(\alpha+\beta/3)$, where α and β are the percentages of α and β fractions found by analysis. It must be remembered that the relative antiseptic powers of two sub stances such as these α and β resins will vary according to the conditions under which the test is made Thus, for example, whilst the α resin may be three times as potent as the *β resin in wort at p_H 5 4, at p_H 4 3 it is over ten* times as active The function of these resins in brewing is to check the growth of bacteria which may gain access during any stage of the process subsequent to the sterilisation of the wort by boiling Checking of the growth of the organisms in the early stages of their multi plication is valuable, since, with fall in the value of p_H of the wort during fermentation the free acidity or hydrogen ions assist the antiseptics In general bacteria grow much less rapidly at p_H 4 than at p_H 5 or 6 However, as regards the relative antiseptic powers of the α and β resins, the matter is still more difficult to follow, for it is as yet not known for certain to what extent these resins respectively are extracted and destroyed during the boiling process. Of the *antiseptic potency possessed by the hops* as used, under normal boiling conditions 50% is either destroyed or not brought into solution, and about 20–30% is lost during fermentation.

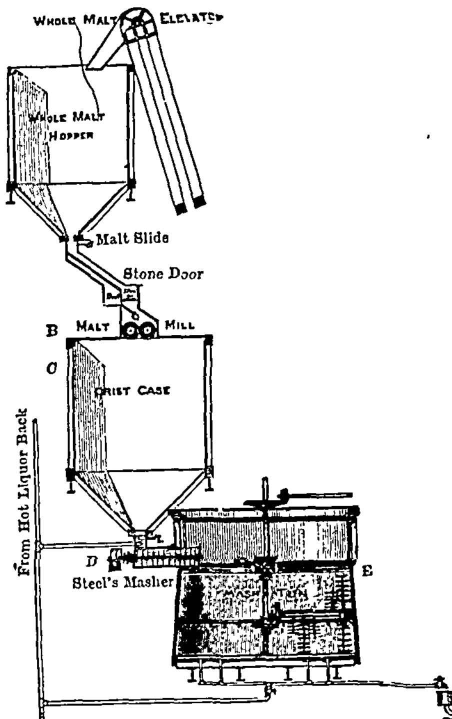
Rapid deterioration occurs during kiln drying and storage of hops. Such loss of antiseptic potency, expressed as percentage of that of the original green hops, is of the order of 60% during kiln drying and 6–20% during a year in cold store (Walker, J. Inst. Brew. 1932, 38, 204; W. Windisch, P. Kolbach and C. Vogl, Woch. Brau. 1931, 48, 501). During storage the α-acid is slowly converted into matters which go to swell the β fraction. It is possible that micro-organisms such as *Mucor spinescens* (Lindner), *Penicillium expansum* (Link), *Aspergillus niger* (Van Tieghem) are concerned in this loss of preservative power (A. H. Burgess, J Inst. Brew. 1935, 41, 467).

In practice hops are valued by both the empirical hand valuation and by determination of the resins, the antiseptic or preservative value being expressed by the formula $10(\alpha+\beta/3)$. Hand valuation is based on aroma, signs of damage, particularly that due to moulds, quantity of "condition" or resin rubbed on to the palms of the hands, "balling" when pressed, appearance and number of seeds, etc. Expert valuations have shown very fair agreement with laboratory determination of antiseptic power (J. S. Ford and A. Tait, J. Inst. Brew. 1932, 38, 351 ; 1926, 32, 19).

Hops are sometimes contaminated by arsenic derived from the fuel used in the kilns in which they are dried. To avoid this, hot air is often used, the actual combustion products not *coming into contact with the hops. Hops are* usually exposed to sulphur dioxide when drying on the kiln. This improves their colour and otherwise appears to have no ill effect. Free sulphur is also found in hops; this is due to the application by spraying of sulphur to the hop plant for the prevention of mould, or may possibly occur when sulphuring hops on kiln by incomplete combustion and volatilisation of some sulphur. Sulphur is transformed by yeast into sulphuretted hydrogen, which, if intro duced into the finished beer, may spoil the flavour It may be detected and estimated by the amount of stain produced by the evolved gases on lead paper.

The development of the downy mildew in recent years has caused considerably anxiety to hop growers. Spraying with Bordeaux *mixture* at the appropriate stages in the growth of the plant has been recommended as a means of combatting the mildew, and much success has resulted (E. S. Salmon and W. M. Ware, J. Inst Brew. 1932, 38, 37).

Brewing Processes.—These processes begin with grinding the malt (*see* Fig. 3). If the latter were perfectly modified, mere crushing between two plain rollers would suffice, and in some breweries, good malts being available, this is done. *However, even the best malt* treated in this way will be imperfectly extracted, and starch may be found in the residue of grains remaining in the mash tun after extraction is completed. This is due to the fact, as has already been described, that dissolution of the cell wall proceeds from the proximal *to the* distal end of the grain ; and that as even the finest barleys do not germinate absolutely evenly, to avoid excessive loss from overgrown corns, the process must be stopped in many corns before its completion, so that there must inevitably be a number of corns possessing "steely ends."



If, in order to reduce these " steely ends " to a condition in which they will dissolve in the mash tun, they are finely ground, the filtration would be so slow as to make the process unworkable. Mills have therefore been devised in which the roughly crushed malt is separated by sieves and air currents into various portions, and the grits and hard ends finely ground and remixed with the remainder of the crushed malt. Fig. 4 illustrates a modern malt mill.

The grinding is usually preceded by treatment in cleaning machinery, in which the malt is brushed, beaten, exposed to a current of air, and sieved. Thus stones, surface dirt, straw, weevily (empty) corns and other foreign bodies are removed. Fractionation by varied air currents is also practised. If the malt contains over about 4–5% of moisture, an inadequate grind is effected, and extract is lost. For this and other reasons such malt is redried before grinding. It is customary for British brewers to use more than one type of malt in any one brew, usually a two-rowed and a six-rowed type *being blended. These may be ground separately* with appropriate settings of the mill rollers, and

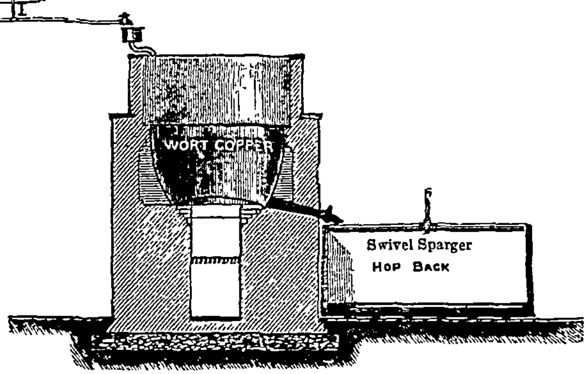


Fig. 3.

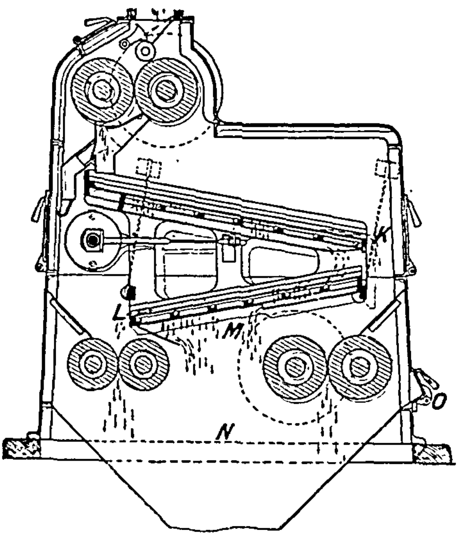


Fig. 4.

delivered to separate compartments of the grist case. Alternatively, they may be mixed, graded by sieving machinery, and the grades so treated. Small or narrow corns of the two-rowed variety are thus ground along with corns of similar size from the six-rowed type.

The ground malt is collected in receivers (malt hoppers or grist cases) until the amount required for the brew is complete. These receivers command the mash tun, the vessel in which the malt and water are mixed.

Mash tuns (Fig. 5) are made of wood, wood lined with copper, wrought or cast iron, and consist of roughly cylindrical vessels fitted with false bottoms of perforated metal plates. Pipes are connected with the real base of the tun for drawing off the clear liquid (wort), the spent grains being held back by the false bottom. There is also a chute for expelling the spent grains, and an underlet should be provided for admitting hot water under a low hydrostatic pressure beneath the false bottom. The mixing gear (rakes) in the upper part of the tun is often not needed nowadays, since adequate mixing of

grist and liquor is effected by an external mashing plant, situated above and to one side of the tun (Fig 6). Before running the grist and water simultaneously through the external masher, the false bottom of the tun is covered with water The grains, after mashing, are

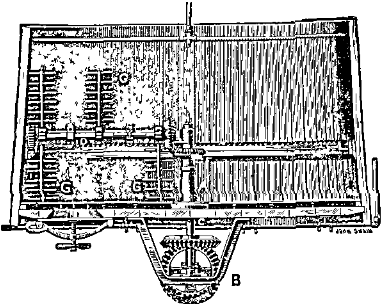


Fig 5.

washed or sparged with hot liquor sprayed on to them from rotating horizontal pipes containing several small holes

Infusion mashing, as practised in Great Britain, consists in mixing water or mash liquor at about 70° (158°F.) with grist at ordinary temperature to yield a mash at about 65 5°

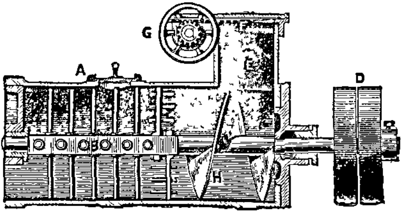


Fig. 6.

(150° F.) and maintaining the latter at this temperature with little or no change for about two hours. Most of the extract (about 95%) passes into solution in the first half hour, but to obtain a satisfactory yield of extract, *i.e.* for reasons of economy, two hours' extraction is needed. Sometimes the initial temperature is slightly lower than normal and it is raised after about twenty minutes by means of the underlet.

Much of the success of brewing depends on the composition of the wort produced and sent forward for fermentation. The factors which influence the composition of the wort, *i e.* the quantity and quality of the extract, are the following:

(1) The nature of the grist, *i.e.* the proportion of malted to non-malted grain, and the diastatic activity of the mixture. The diastatic activity referred to here includes the dextrinising as well as saccharifying form With increasing total nitrogen concentration in the malt there is an increasing concentration of permanently soluble nitrogen in the wort. Amino- and amido-nitrogen are scarcely affected (L R. Bishop, J. Inst. Brew. 1931, **37**, 345). Maize contributes very little nitrogen in soluble form (R H. Hopkins and J. A. Burns, *ibid.* 1930, **36**, 16)

(2) Temperature, particularly at the time of completion of admixture in the external masher: the highest temperature reached will control the destruction of enzymes and therefore the amounts to survive, the permanent temperature, the rates of action promoted by such enzyme activities as survive. Under normal conditions the highest quantity of extract is secured at 65°–71° (150°–160°F.), of maltose at 62°–65° (144°–150°F.), and of permanently soluble nitrogen at 50°–55° (122°–131°F.) (H.T. Brown, J. Inst. Brew. 1909, **15**, 205; L. R. Bishop, *ibid.* 1931, **37**, 353; J. H. Oliver, *ibid.* 1929, **35**, 191; H. E Kelly, *ibid.* 1932, **38**, 440; W. Windisch, P. Kolbach, and E. Schild, Woch. Brau 1931, **48**, 253–298).

(3) Duration of mash, mainly a quantitative factor.

(4) Concentration of mash. This is usually about 2–3 barrels per quarter, *i e.* 2 1–3·1 parts of liquor to 1 of malt. Increasing concentration of grist in the mash is accompanied by increasing percentages of maltose and of nitrogen in the wort solids. More grist than 1 in 6 of water

leads to lower quantity of extract passing into solution (H. Schjerning, Compt. rend. Trav. Lab. Carlsberg, 1913, **9**, 237; J. H. Oliver, J. Inst. Brew. 1929, **35**, 191).

(5) p_H of mash. The optimum value of p_H for extract yield is about p_H 5·2, measured in the wort, for permanently soluble nitrogen p_H 5·0–5·2, for maltose p_H 5·1–5·4. These values apply to mashing temperatures of about 65° (150°F.) (R. H. Hopkins, J. Inst. Brew. 1925, **31**, 399; G. Hagues, J. Inst. Brew. 1924, **30**, 905; W. Windisch, P. Kolbach, and L. v. Benedek, Woch. Brau. 1929, **46**, 345; H. E. Kelly, J. Inst. Brew. 1932, **38**, 440).

(6) Temperature and duration of sparging. Sparging is usually continued until the "runnings" have fallen in specific gravity to about 1003–1005. The solids extracted from the spent grains in the later stages contain less maltose, more nitrogen, and more mineral matter than the original extract. Sparging, too prolonged or at too high a temperature, over 80° (176°F.), extracts glutinous matter which may cause haze. High sparging temperatures may, however, be used in stout brewing.

Under British mashing conditions about half as much more nitrogen is brought into solution than was previously soluble in cold water. Of the wort carbohydrates about 12–15% is cane sugar, glucose and fructose, 55–65% is maltose, the remainder, 20–30%, dextrins. The latter are only slowly, and in very small degree, fermentable.

The temp. of the mash is controlled empirically, but it should be remembered that a contribution of heat equivalent to 5°–6° (9°–11°F.) is made by the "slaking heat" of malt containing 2% of water. Slack malt yields less slaking heat.

The decoction system, practised in "lager" brewing, involves in principle, initial mashing at a low temperature, *e.g.* 35°–40° (95°–104°F.) to extract enzymes and initiate protein conversion, followed by a succession of stands at such temperatures as 50°, 60°, 75° (122°, 140°, 167°F.) for the purpose of promoting respectively peptonisation of proteins, maltose formation, and complete extraction of the grains. The temperature is raised each time by withdrawing about one-third of the mash and boiling it in a separate copper from which it is pumped back. There is thus adopted a systematic treatment designed to obtain in the wort all the substances which are needed, peptones to contribute palatableness and head retention to the beer, maltose to produce alcohol, and full quantitative yield of extract. It is seen now why maltsters on the Continent do not need to secure such complete modification as is necessary for infusion brewing, and also one reason why 5–6% of moisture often present in their malts does not give rise to instability in the beer.

From approximately 30 to 40% of the malt nitrogen is rendered permanently soluble in infusion mashing, Californian malts yielding the lower, and some varieties of home malts, particularly if the total nitrogen content is low, yielding the higher percentage. At 50° (122°F.), the temperature at which the decoction brewer stands his mash for "protein rest," rather more nitrogen is dissolved, and, more particularly, it is degraded to a less complex condition.

Instead of separation of the spent grains from the wort in the mash tun, it is sometimes effected by passing the whole mash through a filter press or mash filter. These, used mostly abroad, are the means of time saving and are economical in that a high extract is yielded especially because more finely ground malt can be used. Too fine a grinding for mash tun purposes would spoil the grains as a filtering medium.

The spent grains or "draff" are disposed of as cattle food. The composition of dried grains is such as the following:

	%
Moisture	4–10
Oil	7–9
"Albuminoids" (N×6·25) .	19–23
Fibre	15–20
Digestible carbohydrates .	41–45
Ash	3–6

The wort, "sweet wort," flows from the mash tun through "draw off" pipes to a collecting vessel called the under back. The pipes must be numerous enough and so distributed as to secure adequate washing of all the grains. From here it passes to the copper, where it is boiled.

Coppers may be heated by fire or steam (jacketed or fitted with steam coil "calorifiers" or both), and may be open or closed. Sometimes boiling is carried out under pressure. Steam heating is economical, and nowadays a satisfactory agitation, which is important, can be effected in steam-heated coppers. Steam pressure and wort temperature can be controlled easily. Boiling is continued for two hours usually, sometimes more, and the later runnings of weaker wort from the mash tun are similarly boiled in a "second" or even "third copper." Mild ales receive about 1 lb. of hops per barrel (1 barrel=360 lb. water, about 350 lb. at boiling), bitter beers about two or three times as much, strong beers more than light ones, lager less than infusion beers. Boiling, in addition to concentrating the wort, which is often necessary, extracts bitter and preservative matters from the hops, coagulates certain wort proteins, destroys the enzymes, sterilises the wort and completes reactions between salts such as calcium sulphate and secondary potassium phosphate, the p_H falling in numerical value as a rule. Conditions necessary to a good "break," or coagulation in large flocks leaving a bright wort, include p_H 5·0–5·5, adequate agitation, and, perhaps, suitable handling of the hops (R. H. Hopkins, J. Inst. Brew. 1925, **31**, 399; G. Hagues, *ibid.* 1927, **33**, 262; H. Lüers, Z. ges. Brauw. 1920, **43**, 51). Some brewers add only a small proportion of the hops as the copper is filling up—they help to prevent "fobbing"—and defer the addition of best hops until perhaps half an hour from the finish. Theoretical considerations support this, as the protein coagulation appears to be better in the absence of hop tannins, and the preservatives of the hops are destroyed (as preservatives) during boiling as rapidly as fresh ones are being extracted.

After boiling, the contents of the coppers are emptied into the "hop back," a vessel furnished with a false bottom of perforated plates which serve to hold back the spent hops. The latter

act as a filtering medium and remove proteins and other matters precipitated during boiling. The spent hops are either "sparged" in a manner similar to the practice in the mash tun, or they are pressed dry in a hydraulic press. In any case the spargings or pressings follow the main bulk of the wort to the next stage of the process. Spent hops are often used as a fertiliser. Dried hops contain about 22% of protein and 35% of digestible carbohydrates (J. L. Baker and H. F. E. Hulton, J. Inst. Brew. 1917, 23, 455).

The hot wort as it leaves the hop back should be perfectly bright. It has now to be cooled, a process which requires far more attention than might be expected. If it were allowed to cool in a deep vessel, without any movement, a *haze* would form which consists of particles too small to be removed, for example, by ordinary filtration or centrifuging in the laboratory (H. T. Brown, J. Inst. Brew. 1913, 19, 84). These particles appear to consist of gluten and of protein-tannin compounds, contain about 10% of nitrogen, and are soluble in dilute alkali but re-precipitated by acid. Particles of calcium oxalate also appear; these collect, to some extent, as a scale on the cooling vessel. All of these matters continue to deposit not only during cooling but throughout fermentation and storage of the beer. Although the amount is minute, the liability of this matter to clog the yeast by adsorption on to the cell surfaces, and to cause haze in the beer and difficulties in clarification of the latter, render its removal of the greatest importance. The secret of success lies in the system of cooling adopted, particularly cooling through the range of temperature below 50° (120°F.).

The first stage of cooling is effected in large vessels, usually open to the air, sometimes closed. Formerly these were shallow, open vessels, but nowadays vessels of any depths may be employed. A certain amount of deposit, "cooler grounds" or sludge, is left behind on the cooler when the wort is run off to the refrigerator. The latter consists of tubes over which the wort flows and through which cold water flows as a countercurrent, and may be either of a vertical or horizontal type. Agitation, while cooling on vertical refrigerators between the temperatures 50° and 33° (120° and 90°F.), is found to help considerably in the flocculation of the minute particles into large ones. The flocculation effected is, however, not so much a consequence of agitation as a surface effect. Quite good flocculation can be secured with comparatively little agitation, while the wort is cooling through the critical temperature zone, provided that a relatively large surface of the wort is exposed, either to the air or to the containing vessel. The critical temperature is considered to be 33°–16° (90°–60°F.) by E. R. Moritz (J. Inst. Brew. 1921, 27, 565; *see also* C. Ranken, *ibid.* 1922, 28, 154; W. J. Watkins, *ibid.* 1927, 33, 67). Failure to secure adequate flocculation is considered to result in the minute particles of tannin-protein and other matters being deposited on the surface of the yeast cells. This hinders the diffusion of crystalloids into and out of the cells and slows down fermentation with disastrous results.

Oxygen is dissolved in the wort when the latter is nearly cooled, about 5–7 c.c. per litre may be dissolved. A certain quantity is almost certainly necessary for healthy yeast growth. It is very doubtful whether "hot aeration" is of any significant value (C. Ranken, J. Inst. Brew. 1925, 31, 73). Enclosed wort refrigeration under sterile conditions should not eliminate cold aeration entirely, but often restricts or eliminates hot aeration without any apparent ill effects. If open refrigerators are employed some device for filtering the air admitted to the room is often adopted to reduce or prevent infection by wild yeasts or bacteria. Until the temperature falls below 55° (130°F.) there can be little or no infection. Coolers are sometimes dispensed with, and the wort runs directly from hop back to refrigerator and is thus rapidly cooled. This is effectual in reducing infection, but it has been found sometimes to lead to faulty clarification (*v. supra*).

Infection of the wort during refrigeration must be primarily derived from the air (dust particles), but in practice it is found, in all but exceptional cases, that air infection is very small and unimportant compared with vessel infection. If the coolers are made of metal there should be little difficulty in keeping these sterilised, as the hot wort every time it covers them should do this; if they are wood it is found that, however well made, sterilisation is impossible. Owing to its porous nature organisms live in the pores just below the surface, and the non-conducting nature of the wood prevents any but the immediate surface layers rising to the sterilising temperature. The same is true of wooden fermenting vessels and casks.

The refrigerators, with the necessary pipe connections, are metal, and it appears at first sight that there should be no difficulty in keeping these sterile, but owing to crevices at joints, etc., in practice the attainment of complete sterility is impossible.

The flocculated hopped wort runs from the refrigerator into the fermenting vessels at about 14°–16° (58°–61°F.). For lager beer it must be further cooled on the refrigerator, down to 5°–6° (41°–43°F.), brine pipes being used. Fermenting vessels are made of certain suitable types of wood, of wood lined with copper or aluminium or coated with carbon enamel preparations. Stainless steel vessels are coming into use. Occasionally stone, slate or concrete is used, and glass lined vessels are favoured by some. It is important that they can be kept clean and sterile and appropriate means to this end have to be adopted with vessels of the respective materials mentioned. Temperature is controlled by cold water pipes, "attemperators," which in lager breweries must be brine chilled.

While the vessels are filling up, and the appropriate quantities of stronger and weaker worts from the various copper "lengths" and hop back spargings are being run into the respective vessels to give worts of the desired original gravities, the "pitching" yeast is added, at a rate of about 1 lb. of pressed yeast per barrel, or 0.3%. The yeast is obtained from a previous brewing. The number of yeast cells added is very much greater than the number of

organisms with which the wort is normally infected. The amount, however, must be so regulated, according to the nature of the wort, that a considerable increase (5–10 times) is possible. The yeast *Saccharomyces cerevisæ*, used by brewers, is a "culture" yeast, that is, one which has been selected or possibly evolved in civilised communities as specially suitable for brewing.

There are two main varieties—"high" or "*top*" *fermentation* yeast, and "low" or "bottom" fermentation yeast.

The first is used at a higher temperature than the second; the brewery fermentations are consequently more rapid; the yeast rises to the top towards the end of the fermentation, whereas under the conditions in which the latter is used it falls to the bottom at the end of the fermentation. British beer is brewed on the top fermentation system, almost all other beer on the bottom fermentation system.

As worts usually become infected by other yeasts (wild yeasts) and bacteria during the cooling and subsequent processes, the yeast crop obtained at the termination of fermentation will contain foreign organisms. As this is used for seeding the succeeding worts, it is possible in time for the seed yeast to become seriously infected, even if the initial wort infection is kept down by suitable precautions. As will be seen later, these foreign organisms may lead to serious defects in the final product.

In order to surmount this difficulty, Hansen in 1883 introduced his pure yeast system into bottom fermentation breweries. He separated single yeast cells from the brewery yeast, and from each of these grew sufficient to make a trial brewing. The culture giving the most satisfactory result was selected and used in the brewery. A pure pitching yeast was thus obtained. This has been adopted with great success in lager beer brewing, but breweries working on the top fermentation system have not found the pure yeast thus prepared altogether satisfactory. Many reasons have been given for this. It is fairly well agreed that the explanation of its non-success is that a mixture of yeast is necessary in this case, although there is much diversity of opinion as to what this mixture should be (G. H. Morris, J. Inst. Brew. 1900, **6**, 333; N. H. Claussen, J. Inst. Brew. 1904, **10**, 308; R. L. Siau, J. Inst. Brew. 1906, **12**, 118; H. Schionning, Compt. rend. Trav. Lab. Carlsberg, 1908, **7**, 138; J. Inst. Brew. 1909, **18**, 2; B. M. Brown, J. Inst. Brew. 1934, **40**, 9). Yeast may be freed from bacteria by treatment with solutions of definite acidity, about 0·1% H_2SO_4 (H. T. Brown, J. Inst. Brew. 1916, **22**, 328).

In Great Britain as soon as the vessels are filled, and before fermentation, excise readings of volume and original gravity are taken. Two objects must be achieved in the fermenting vessel, apart from the prevention of infection. Firstly, the wort must fall, with reasonable rapidity, from its original specific gravity to about one-third or as low as one-fifth of this value according to type of beer, a corresponding production of alcohol taking place. Secondly, a good and adequate crop of healthy yeast must form and separate properly.

The rate of fermentation at any instant, assuming that the yeast is uniformly mixed with the wort, will depend on many factors. Firstly, the fermentative power of the yeast, which depends on its physiological state. The extent to which matters are deposited on the cell surfaces may possibly interfere with diffusion (H. T. Brown, J. Inst. Brew. 1913, **19**, 84). Secondly, the concentration of the yeast to which the rate of fermentation is directly proportional over limits far wider than any occurring in the fermenting vessel. This is easily seen to be the case if one regards each yeast cell as a unit producing an equal amount of alcohol in unit time. Rate of fermentation is proportional to weight of yeast, although large cells function faster than small ones. The concentration of yeast in the wort is influenced by its distribution in and on the wort, which in its turn is influenced by suspended matter present (C. Ranken, J. Inst. Brew. 1927, **33**, 76; C. Ranken and J. R. Bell, *ibid.* 1928, **34**, 265). Thirdly, the concentration, but not the nature, of the fermentable sugars present. The monosaccharides, glucose, fructose and mannose, the disaccharides sucrose and maltose all appear to be fermentable at approximately the same rate under the same conditions, and this rate is nearly independent of the sugar concentration between about 1 and 10% (A. J. Brown, J.C.S. 1892, **61**, 369; A. Slator, J.C.S. 1906, **89**, 128; 1908, **93**, 217; R. H. Hopkins and R. H. Roberts, Biochem. J. 1935, **29**, 919, 931). Only when "attenuation" or fall in gravity is nearly as complete as possible, *i.e.* within four degrees of the limit, will sugar concentrations *per se* influence the rate of fermentation. Fourthly, temperature; for a rise of 5° (9°F.) in temperature, *i.e.* about the total rise occurring during fermentation in brewing practice, the rate of fermentation increases to about twice (A. Slator, *ibid.*; R. H. Hopkins and R. H. Roberts, Biochem. J. 1935, **29**, 2486). Mineral salts and p_H over the range normally occurring in brewers' worts during fermentation, viz. p_H 5–4, have comparatively little influence on the rate of fermentation.

Of the factors considered above, those which merit consideration are the first and second. Temperature, p_H, and sugar concentration do not vary from brew to brew sufficiently to make any significant difference. The yeast will remain free from clogging of the cell surfaces if adequate flocculation on the refrigerator has been secured, if not, a sluggish secondary fermentation results, and trouble is likely to follow, as micro-organisms pathogenic to beer such as wild yeasts and bacteria may be growing more rapidly. The fermentative activity will also depend on the previous history of the yeast, the type of wort in which it was grown, how it has been stored, etc. In so far as rate of fermentation depends on the concentration of yeast, this latter factor is also the concern of the brewer, from the point of view of his yeast crop.

The amount of yeast in the wort at any instant depends on many factors. When a small seeding, *e.g.* 0·3% of pressed yeast, is introduced into wort, there is a short lag phase with little or no cell increase, followed by a logarithmic phase,

during which one cell becomes two, two become four, and four become eight in equal intervals of time. This time interval, termed a generation time, is about four hours at 18° (65°F.) (mean brewing fermentation temperature) but is only 83 minutes at 30° (86°F.) (A. Slator, Biochem. J. 1913, 7, 197; 1918, 12, 248; A. Tait and L. Fletcher, J. Inst. Brew. 1923, 29, 509). Later, inhibition of rate of multiplication sets in, due to accumulation of alcohol, carbon dioxide, etc., and finally, approaching exhaustion of sugar brings multiplication to a standstill. The views expressed by certain workers on the subject of rate of multiplication are not all in agreement, but the differences have been due largely to the difficulty of deciding when a yeast bud becomes a new cell (*see also* H. T. Brown, Ann. Bot. 1914, 28, 197; R. H. Hopkins, J. Inst. Brew. 1927, 33, 337). Oxygen is necessary for adequate growth and health of the organism; thus, for instance, half fermented wort, saturated with carbon dioxide and protected from access of oxygen, is deficient in this respect. A. J. Brown (J.C.S. 1905, 87, 1395) considered the presence of oxygen in the original wort (H. T. Brown, *ibid.*) to be essential for yeast growth. Whilst a very large excess of oxygen enormously increases yeast growth, extremely little is actually necessary for health and normal multiplication (F. Windisch, J. Inst. Brew. 1931, 37, 561). It is largely a matter of oxidation reduction balance, or the value of r_H of the system. A high value of r_H, that is a high oxygen intensity, is essential to the respiration of yeast, and development by this means is inhibited if the oxygen intensity falls, that is, r_H decreases. So far as yeast development in the finished beer is concerned, this is slow if the value of r_H is below 15, a value approximating to that at which methylene blue is decolourised (J. de Clerck, J. Inst. Brew. 1934, 40, 407; F. Mendlik, Woch. Brau. 1934, 51, 305).

The essential nutrients of yeast include potassium, magnesium, calcium, traces of iron, very minute traces of copper and possibly of other metallic ions, phosphate, sulphate, nitrogen in any of a number of suitable forms, and any one or more of a number of assimilable sugars such as maltose, sucrose, glucose, etc. The nitrogen may be in the form of ammonium salts, amino acids, amides, etc., or a mixture of these with more complex protein degradation products. In wort it is the last named condition which obtains, and significantly enough, much better yields of yeast as regards both quantity and quality are obtained from wort than from a synthetic mixture. There are a number of reasons contributory to this. For instance, to secure a good growth in a given nitrogenous nutrient, the optimal p_H for that nutrient should be employed. According to F. Ehrlich (Ber. 1907, 40, 1029) yeast splits ammonia and carbon dioxide from amino acids, an alcohol being formed which is of no use to (and may help to inhibit the growth of) the yeast. Thus,

l-leucine+water yields inactive *iso*amyl alcohol +carbon dioxide+ammonia

$$CHMe_2{\cdot}CH_2{\cdot}CH(NH_2)COOH+H_2O$$
$$=CHMe_2{\cdot}CH_2{\cdot}CH_2OH+CO_2+NH_3$$

The ammonia thus formed is utilised for yeast growth. The yeast manufacturer grows his yeast in ammonium salts as source of nitrogen, special conditions being necessary for good yields. In some ways brewers' wort simulates these conditions. It is highly buffered and prevents the attainment of a reaction at which inhibition would be serious. It has been found that, if alcohol concentration is kept below 4%, growth of yeast in wort continues until the p_H has fallen to 2·15, but restoration of normal p_H (4–5) is followed by fresh growth (V. Hartelius, Compt. rend. Trav. Lab. Carlsberg, 1934, 20, No. 7; *see also* A. L. Stern, J.C.S. 1899, 75, 201; 1901, 79, 943; A. Tait and L. Fletcher, J. Inst. Brew. 1922, 28, 597; C. Taxner, *ibid.* 1935, 41, 27; R. H. Hopkins, *ibid.* 1935, 41, 30). Lastly, minute quantities of "bios" first discovered by Wildiers, and now usually called "growth-promoting factors" are necessary. N. Nielsen and V. Hartelius (Compt. rend. Trav. Lab. Carlsberg, 1932, 19, No. 8; 1934, 20, No. 1) have succeeded in establishing the existence of at least two growth-promoting factors, A and B, the latter of which occurs in wort. R. J. Williams and D. H. Saunders (Biochem. J. 1934, 28, 1887) find that the yeast growth factor *pantothenic acid* previously isolated by Williams, active as it is, is even more active in conjunction with inositol, "Bios I," or vitamin B, or both, whereas the latter two exert relatively little effect. Normal wort contains an excess (except in the amount of sugar) of all the substances, including growth-promoting factors, necessary for yeast growth.

To indicate the practical significance of all that has been stated above, the seeding (pitching) of a brewery wort with 10 million cells per c.c., i.e. about 2·5 g. of pressed yeast per litre (the usual proportion), will be followed by a period of quiescence before growth starts. The cell vacuoles disappear if the wort is strong. Growth then proceeds steadily but retarding influences soon come into action and continually slow down the rate. The chief of these is the effect of carbon dioxide and the gradual failure of the oxygen supply, *e.g.* in one experiment, saturation with carbon dioxide reduced the rate of yeast increase by about 22% (A. Slator, J. Inst. Brew. 1923, 29, 817). There is plenty of yeast food present, and the amount of alcohol is not sufficient to have any great influence. Rapid fermentation is now taking place, with evolution of large quantities of carbon dioxide which prevents air getting into the fermenting solution. It is at this stage of the fermentation that brewers who employ two fermentation vessels (*see below*) usually "drop" or "tun," that is, transfer the fermenting worts from the one vessel to the other. This causes the removal of some carbon dioxide, and allows some air to be absorbed by the worts, there is a slight renewal of yeast growth; but the chief amount of yeast increase has now taken place. The rate of fermentation is now mainly dependent on the number of yeast cells and temperature.

The influence of temperature is great, as already indicated; the following table gives the

grams glucose fermented per second by 10^{14} yeast cells (Burton yeast) :—

Temp.	g.
40° C.	5·05
30° C.	3·00
20° C.	1·30
15° C.	0·68
5° C.	0·140

The temperature continuously rises from 15°–20° (60°–68°F.) (top fermentation) owing to the heat evolved by fermentation: the heat of fermentation of glucose is 24 Kg. Cals. (A. Bouffard, Compt. rend. 1895, **121**, 357; A. J. Brown, J. Inst. Brew. 1901, **7**, 93), and the brewer has to control this by his attemperators. Although the sugars present in wort are fermentable individually at approximately the same rate under the same conditions, except that at 15° (60°F.) maltose may with some yeasts be rather more slowly fermented than the other sugars, nevertheless the yeast selectively ferments glucose faster than fructose in mixtures of the two. The residual unfermented but fermentable sugar in beer is likely therefore to be relatively rich in fructose, a very sweet sugar. The fructose is derived from the sucrose in the malt, added sucrose or invert, and from priming solutions, if added.

The mechanism of alcoholic fermentation is now fairly clear, although some matters still need elucidation. In 1897 Buchner expressed yeast juice from yeast and found it to be capable of promoting alcoholic fermentation. A. Harden and W. J. Young discovered the influence of phosphates (Proc. Roy. Soc. 1906 (B), **77**, 405; 1910 (B), **82**, 321). R. Robison isolated the hexose monophosphates (R. Robison and W. T. J. Morgan, Biochem. J. 1930, **24**, 119; R. Robison and E. J. King, *ibid.* 1931, **25**, 323).

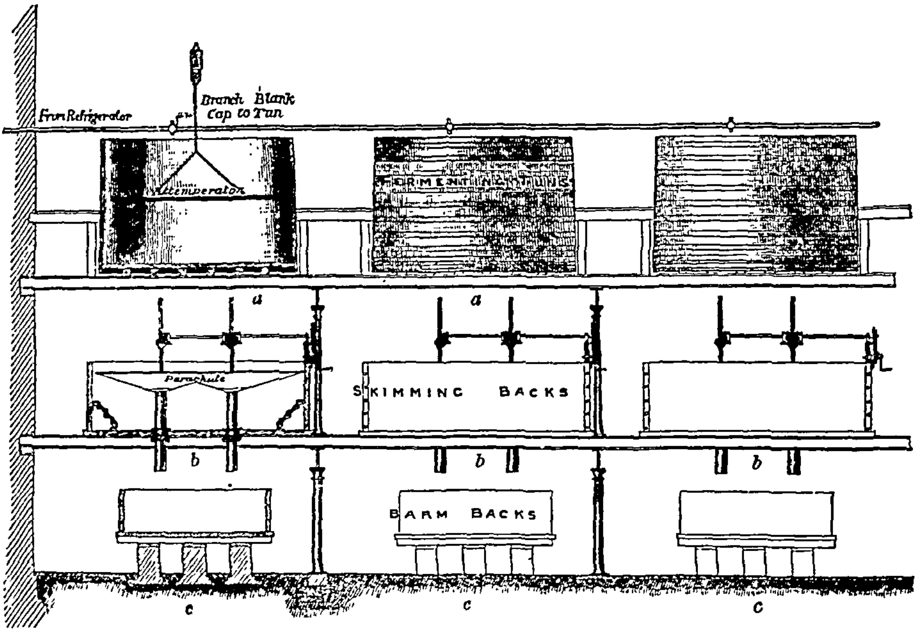


FIG. 7.

C. Neuberg and J. Kerb (Biochem. Z. 1912, **47**, 405; *ibid.* 1913, **58**, 158) and others found that pyruvic acid is clearly an intermediate product in the breakdown of hexoses, and developed the hypothesis associated with the name of Neuberg which was an essential step in progressing to our present-day theory. Finally G. Embden and O. Meyerhof developed the latter, which is as follows. Hexose diphosphate reacting with glucose and inorganic phosphate yields phosphoglyceraldehyde, which, until some acetaldehyde has been formed, undergoes simultaneous oxidation and reduction yielding phosphoglyceric acid and glycerophosphoric acid, the latter of which then splits off phosphoric acid to form glycerol, which is always formed in alcoholic fermentation. The phosphoglyceric acid also splits off phosphoric acid to form pyruvic acid, from which carbon dioxide is removed to leave acetaldehyde. Immediately the latter compound appears it is reduced to alcohol at the expense of the phosphoglyceraldehyde, which is oxidised to phosphoglyceric acid, and this re-enters the cycle to produce more pyruvic acid, and so on.

The enzyme *zymase* of yeast juice is complex and, apart from *co-zymase*, which can be separated by dialysis, contains *carboxylase* and *phosphatases*. The influence of inorganic phosphates on fermentation by yeast juice is not reflected in fermentation by living yeast. The products of alcoholic fermentation of maltose in practice are about 51% of ethyl alcohol, 49% carbon dioxide, 1 or 2% of glycerol, small amounts of the sugar being taken up for yeast nutrition, the whole totalling 105·5, to which quantity of glucose 100 parts of maltose are equivalent. The other products, succinic acid, higher alcohols, etc., are by-products of yeast metabolism.

From 25 to 40% of the total wort nitrogen is removed during fermentation, in brewery practice. As much as 60% can be removed by laboratory procedure involving addition of extra sugar, etc. No doubt some of the colloidal forms are adsorbed on to the surface of the yeast cells, but mostly it has been assimilated. Possibly, even under brewery conditions, a certain quantity is excreted by the yeast, so that the quantity disappearing during fermentation represents a balance between adsorption and excretion. The value of p_H falls from about 5 to about 4, this being due to production of acid and removal, by the yeast, of buffering matters.

The first sign of fermentation in the fermenting vessel (*see* Fig. 7) is the appearance of a froth bearing a scum. This contains a little yeast and some resinous and albuminous matter and is skimmed off. In a few hours a "cauliflower" head of foam forms and later gives place to a larger "rocky" head. As yet the main portion of the yeast is in the wort, but, although it has a greater specific gravity, about 1090, than the wort, it is kept in suspension by the rising bubbles of carbon dioxide, but towards the end it flocculates and entangles the rising bubbles, the spongy mass thus formed rising to the surface and forming the yeasty head. If the latter is not quickly removed the gas escapes and the yeast falls to the bottom of the liquid. If yeast be allowed to fall through the fermented wort, it communicates to it a yeasty flavour and spoils it. In bottom fermentation the yeast also flocculates towards the end of the fermentation, which, owing to the low temperature, proceeds much more slowly, and the yeast falls to the bottom of the vessel. The method of removing the yeast, or of "cleansing," has an appreciable influence on the type of beer produced. It will be seen that the rate and conditions of separation of yeast and its removal will affect the amounts of secondary products of fermentation, higher alcohols, esters, etc., which diffuse from the yeast mass into the beer, and also the amount of hop bitters adsorbed by the yeast. These secondary products of yeast metabolism and the hop bitters have a marked influence on flavour.

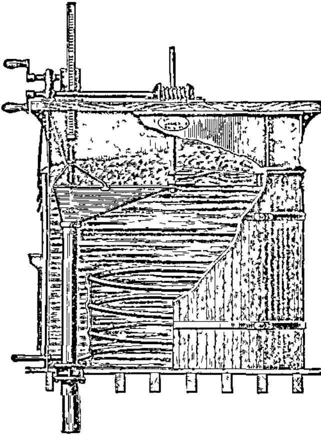


Fig. 8.

From Sykes and Ling's "Brewing" (Charles Griffin & Co. Ltd.)

There are two well defined methods of cleansing employed in Great Britain—skimming (most general) and the "union" system employed in many Burton breweries. For skimming an arrangement called a parachute is fixed in the fermenting vessel. It resembles a large funnel with its outlet pipe communicating with a vessel beneath (*see* Fig. 8). The height of the funnel is controlled by gearing, so that the yeast as it rises flows over the edge through the pipe into a vessel below. In very large vessels this is assisted by the movement of a skimming board. Sometimes the fermentation is commenced in a plain vessel and the wort dropped when about half fermented into the skimming vessel. During the early stages of fermentation *rousing* is carried out from time to time by mechanical means or by forcing compressed air through the wort.

The beer is allowed to remain quiescent for a day or two, a little more yeast settling to the bottom during this time whilst a residual surface covering protects the beer to some extent from infection, aeration, and loss of carbon dioxide. It is now racked into casks, fairly bright but not too bright. The fermentation is so controlled that at the racking stage there always remains some fermentable sugar and some yeast in suspension as whatever mode of yeast removal is adopted, it is impossible to remove all. It is convenient and usual to employ an intermediate vessel (racking vessel). This is provided with taps, usually of special design, so that the casks are filled without loss due to overflow. At racking the beer is too flat for consumption, excess of carbon dioxide having escaped. In cask a type of "secondary" fermentation takes place, residual fermentable sugars and yeast, intentionally left behind in the beer at racking, serving the purpose. Sometimes a small quantity of "priming" sugar, usually cane sugar, invert, or "dextrin maltose," is added to make sure of this.

The union system of cleansing involves running

the fermenting wort into a set of casks, each holding about 150 gallons or more (*see* Fig. 9) mounted horizontally on trunnions on a framework. Each cask is furnished with a swan neck which fits into a socket in the highest portion of the cask, and projects just over the edge of a yeast trough, which is long and shallow and is fixed above the unions. There is a tap at the lowest portion of the cask, the nozzle of which projects a couple of inches into the cask. The tap has a screw thread, so that the inlet can be lowered or the tap entirely removed, leaving the cask opening free. The casks are also provided with attemperators through which cold water may be passed for controlling the temperature of fermentation. Sometimes one large cigar-shaped aluminium vessel replaces several casks, but it has a number of "swan necks." The yeast trough is also provided with attemperators. At one end the yeast trough communicates with the cross trough or feeder by outlets at various levels, any one or all of which may be closed as required. The feeder communicates with the casks by a long side pipe, the feeder inlet of this having a screw cup which may be raised or lowered in order to prevent sediment from the feeder getting into the cask, or the cup may be removed entirely. This pipe is furnished with a main tap to control the flow into the cask (the feed), and each cask has a separate tap, so that any one may be disconnected. There are also outlets from the yeast trough and feeder for removing yeast (barm). The fermenting wort in the unions is under the pressure of the head of wort in the feeder, and consequently so long as carbon dioxide is being produced in quantity a foam is forced up the swan necks into the yeast trough.

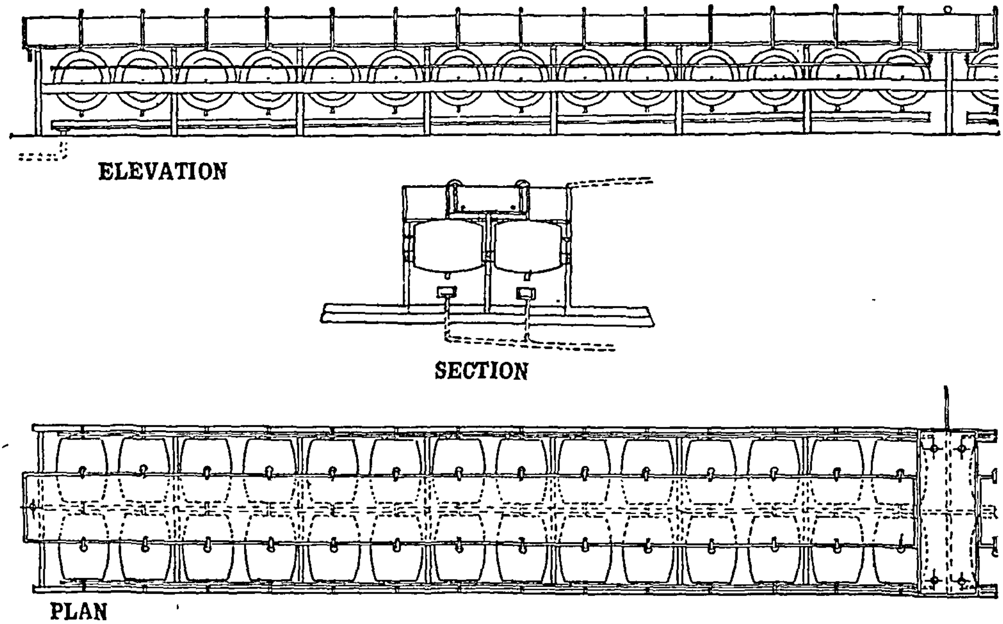


Fig. 9.

This settles to some extent, and furnishes more head of liquor in the feeder, and so the circulation continues. With a wort of fairly high gravity the whole bulk of the brewing would circulate several times. When the fermentation nears the end, the character of the foam in the yeast trough changes. It becomes yeasty, and separates, a part of the yeast settling to the bottom and a part forming a thick skin on the surface; in between these two layers is a stratum of fairly bright beer. This bright beer only is allowed to return through the feeder, where a little more settling takes place, into the casks, so that ultimately the casks become filled with more or less bright beer, and the greater part of the yeast remains in the yeast trough. After allowing the beer time to settle in the unions, it is run into a racking vessel.

There exist modifications of both the skimming and the union systems. What is in principle a modification intermediate between the two is employed in Yorkshire—a system known as the "stone square system," because the fermenting vessels were, and in some cases still are, constructed of stone or slate. More usually, nowadays, they are lined with or made of metals—copper, aluminium or stainless steel. The square top of the vessel is covered except for a manhole in the centre, which is surrounded by a flange. The main vessel is also surmounted by an open one of the same dimensions, except in height, which is much less. Attemperators are lowered through the hole, which also will admit a man to enter the vessel to clean it. The lower vessel is filled up to the top. When fermentation sets in, froth and afterwards yeast are expelled through the hole and collect and settle in the upper vessel, from which the wort, when clear, can be run back through a valve. Pumping is possible for rousing purposes. The fermentation is slow, the temperature range about 16°–19° (61°–66°F.), and a very full drinking

25% of the quantity present at that stage (H. Heron, J. Inst. Brew. 1928, **34**, 377).

Stability of beer is of two kinds, protein stability and biological stability. The former presents the more difficult problem, and is the only one in the case of efficiently pasteurised or filter-sterilised beer. Haze or greyness, due to formation of albuminous matters or these combined with hop products such as tannins, are difficult to control. The lager brewer, whose product has to withstand chilling immediately before its consumption, achieves it as far as possible by peptonisation in mashing and long storage at 0° in his lager tanks.

Biologically, wild yeasts or bacteria may develop in the finished product, causing a variety of possible symptoms. Some organisms do no particular harm. Of the others, wild yeasts cause turbidity, yeast bite, over-conditioning in cask, peculiar odours, or bitterness. It will be recalled that a high value of r_H is necessary for yeast respiration, and that such development is very slow if r_H is below 15, the value, approximately, at which methylene blue is decolorised. If methylene blue is rapidly decolorised by beer, it is unlikely that yeast haze will develop. If there is present any quantity of fermentable sugars, the yeast can develop by fermentation, even if the oxygen intensity or r_H is low, so that two conditions must be satisfied if the development of yeast haze is to be prevented: a low content of fermentable sugars and a low oxygen intensity—exclusion of air.

Bacteria cause turbidity, odours, acidity or ropiness. Cleanliness, particularly of plant, purity of yeast, of air admitted to the refrigerators and fermenting room, can help a great deal. The biological stability of beer, as regards acid-forming bacteria, depends not only on the amount of infection and its virulence (the organisms in imperfectly cleaned casks are likely to be far more virulent than those on dust particles in the air) but on the antiseptic matters present in the wort and beer, derived from the hops (and sulphites). Most bacteria will grow much more rapidly at p_H 5 than at p_H 4, that is in wort than in beer. If no great number have developed before fermentation is complete, and p_H has been reduced to 4, the danger is greatly reduced. The objections to a sluggish fermentation are thus seen. Altogether, the quality of the hops, their handling, cleanliness of plant, and reasonable speed in bringing the beer to a relatively safe reaction, p_H 4 or thereabouts, seem to be the main factors to which attention should be paid. No value of p_H is "safe" for all beers, much will depend also on the other factors mentioned (N. M. Parsons, J. Inst. Brew. 1924, **30**, 30; R. H. Hopkins and J. E. Fraser, *ibid.* 1928, **34**, 387; H. Heron, *ibid.* 1923, **29**, 281; 1924, **30**, 596; J. L. Shimwell, *ibid.* 1935, **41**, 245, 481).

The yeast which is collected at the cleansing operations is usually pressed in a filter press, the beer so obtained being run back into the main bulk. The recovery of yeast pressings is an important feature of brewery economy at the present day, but such pressings should be blended with the beer from which they were obtained. Pressings differ in composition from the beer in which the yeast was formed, especially if any length of time has elapsed between skimming and pressing. The original gravity is higher, mainly, no doubt, as a result of excretion of alcohol from the yeast cells which contain glycogen and the necessary enzymes to ferment it. Whilst alcohol is being excreted there is a simultaneous degradation of nitrogenous matters of the cell which appear in the surrounding medium as higher alcohols, etc. Nitrogen, potassium, and phosphates are higher and p_H is more alkaline. Pressings soon develop bacteria if kept (H. L. Hind, J. Inst. Brew. 1925, **31**, 336; H. W. Harman and J. H. Oliver, *ibid.* 1925, **31**, 353).

Well pressed yeast contains about 73–75% of water, very little of which is located in the interstices of the cells. Unwashed yeast liquefies on storage sooner than washed yeast, and this is ascribed to the removal, by washing, of some factor which accelerates autolysis (A. Tait and L. Fletcher, *ibid.* 1926, **32**, 385).

It has been suggested that yeast washings contain proteolytic enzymes (S. B. Schryver, E. M. Thomas, and S. G. Paine, *ibid.* 1927, **33**, 120). There are three such enzymes in the yeast cell. Firstly, a proteinase which degrades many proteins such as denatured egg and serum albumins, fibrin, casein, gelatin, and certain peptones and which exhibits an optimum activity in the neighbourhood of p_H 5·0; secondly, a polypeptidase which attacks peptides containing a free amino group; and thirdly, a dipeptidase which attacks dipeptides containing both a free amino and a free carboxyl group. The p_H optima of the latter enzymes are between 7·0 and 7·8 (W. Grassman and W. Haag, Z. physiol. Chem. 1927, **167**, 188; W. Grassman and H. Dyckerhoff, *ibid.* 1928, **179**, 18).

Yeast has long been used as a convenient source of vitamin B, a complex food accessory factor now considered to consist of a number of components. Of these, vitamins B_1 and B_2 are susceptible of definite measurement, and the amounts present in yeast vary widely. Apparently some yeasts can synthesise both these factors from nutrient media containing neither (J. C. Drummond and J. M. Whitmarsh, J. Inst. Brew. 1932, **38**, 264). On the whole, it seems probable that brewers' and bakers' yeasts remove the vitamins from the malt media in which they are grown. In consequence, properly fined beer is almost or entirely free from vitamins, although the evidence on this point is conflicting.

Analysis of Brewing Materials and Beers.

Malt.—The determinations normally performed are (1) moisture, (2) extract, (3) colour or tint, (4) diastatic power, (5) cold water extract, and sometimes (6) permanently soluble nitrogen. The processes are empirical and standard methods have been recommended by the Analysis Committee of the Institute of Brewing (*see* J. Inst. Brew. 1933, **39**, 517).

Moisture.—Three hours' drying at 100°C. with precautions. Before the last traces of moisture are removed oxidation and decomposition have become appreciable.

Extract.—Malt, ground in a standard mill, is infused at 65.5° (150°F.) for one hour, diluted to 10% concentration, filtered, and the specific gravity of the filtrate taken. The excess of gravity over 1,000 is multiplied by 3.36, the result being "brewers' pounds" per quarter. Continental analysts mash the malt differently and calculate from the appropriate "Plato" tables the solid content of the wort in "degrees Plato," which is the number of grams of wort solids contained in 100 g. of wort. Actually this table was constructed to represent cane sugar percentages, these being adopted as a standard. If P=the Plato figure so obtained and W=% water in the sample of malt analysed, then 100 g. of malt having been extracted by 800 g. of water, the extract of the malt $=P\times(800+W)-(100-P)$.

To convert the results by the British method, lb. per qr. into the corresponding "Plato" result for the same malt, multiply by the factor 0.802.

Colour of the 10% wort (or of beer) is determined by the "Lovibond" tintometer using the standard colour glasses of the "series 52." To convert the result into the corresponding result by the Continental method, expressed as c.c. of decinormal iodine per 100 c.c., multiply by 0.086.

Diastatic Power.—3 c.c. of a 5% cold water extract of the malt is allowed to act on 100 c.c. of 2% Lintner soluble starch containing 2% of normal acetate buffer mixture, p_H 4.6 for 1 hour at 21° (70°F.). The result of the reducing power determination is calculated to degrees on the Lintner scale.

Cold Water Extract is calculated from the specific gravity of a 5% extract (8% of N/10 ammonia is included to prevent enzyme action during the extraction) prepared at 21° (70°F.) for three hours. By dividing the excess of specific gravity over 1,000 by the factor 0.386, the percentage of soluble solids is obtained.

Permanently soluble nitrogen is determined on the 10% wort prepared in the determination of "extract," after boiling, making up to volume and filtering, using the Kjeldahl or other suitable process.

Raw or prepared grain is analysed for extract by treating 50 g. (previously gelatinised in the case of raw grain) in 300 c.c. of water at 65.5° (150°F.) with 100 c.c. of 25% cold water malt extract at the same temperature, and digesting for two hours. After dilution to 506 c.c. and filtration the specific gravity of the filtrate is determined, and this, after deducting that of a control for the malt extract, is used for calculation in the same way as that employed in malt analysis.

Hops.—Determination of preservative value (P.V.). 10 g., suitably sampled, are extracted with ether in a Soxhlet extractor until at least twelve siphonings have taken place. After evaporating off the ether at 40° the residue is dissolved in methyl alcohol to 75 c.c. Of this, 15 c.c. together with 35 c.c. of 1% sodium chloride are repeatedly extracted with light petroleum, the latter taking out total soft resins—which are recovered and weighed as such. For the α-resin, 40 c.c. of the methyl alcohol solution are precipitated at 60° (140°F.) with a 1% lead acetate in methyl alcohol. The weight of lead salt, weighed in a Gooch crucible, multiplied by 0.63, gives the weight of α-resin. % total soft resins−% α resin=% β resin. $P.V.=10(\alpha+\beta/3)$ (*see* J. S. Ford and A. Tait, J. Inst. Brew. 1932, **38**, 351).

Beer.—Original gravity is the most important determination, and is made by distilling 100 c.c. until about 75 c.c. of distillate has collected. Usually the flask and still used are of "Revenue" pattern. Both distillate and residue are diluted to 100 c.c. and their specific gravities determined. To the specific gravity of the residue must be added the number of "degrees of gravity lost" equivalent to the alcohol in the distillate. This number is obtained from the official table used for revenue purposes, using the difference between the specific gravity of the distillate and that of water (1,000); this difference being known as the "spirit indication." A summary of the table from which interpolations can be made is given here.

Spirit indications	Corresponding degrees of gravity lost.
1	4.25
2	8.50
3	12.90
4	17.30
5	21.85
6	26.40
7	31.00
8	35.65
9	40.30
10	45.00
11	49.85
12	54.85
13	59.95
14	65.10

This table is entirely empirical in origin and the latter is described together with a complete review of the subject by H. T. Brown (J. Inst. Brew. 1914, **20**, 569; *see also* R. H. Hopkins, *ibid.* 1927, **23**, 320).

Sulphur dioxide in beer is determined by distilling 250 c.c. of beer with 100 c.c. of water and 5 c.c. of glacial phosphoric acid in a stream of carbon dioxide. The gas should be passing through the boiling liquid before the beer is run in. The distillate is collected in saturated bromine water and the sulphur dioxide is estimated as sulphate.

Beer is made in most parts of the British Empire, the United States, most European countries, and Japan. The last named country is to-day one of the largest producers. Top fermentation (and infusion) brewing is practised mainly in Great Britain, Ireland, and certain of the Dominions, India, and to some extent in the countries of north-west Europe. A little bottom fermentation (decoction) brewing goes on in Britain, whilst infusion and top fermentation brewing are not unknown, for instance, in Germany. Probably the strongest ale brewed in Britain is of about 1,120 original gravity, but this is rare, most beer ranging from 1,055 to 1,035, similar ranges obtaining in most beer-consuming countries. The word "ale" is

usually confined to infusion products other than stout and porter, whilst "beer" is a more comprehensive term. (Historically, ale referred to unhopped and beer to hopped products.) Mild ale, the more lightly hopped, is usually of lower original gravity than the bitter. Of the beer consumed in England about 40–50% is mild ale, 35–40% bitter, 10–15% stout, and 5% is strong ale. Bottling and pasteurisation are on the increase; in some countries, such as Denmark, most of the beer is pasteurised, some of it in special patent aluminium casks of 5½ gallons capacity. In Germany stainless steel casks are being used, and in America beer is now being "canned" (pasteurised) instead of bottled.

It is of very little use giving the typical results of analyses of beers, except so far as the percentages of alcohol and residual solids are concerned. The quantities of ash, phosphates, etc., naturally increase with original gravity, and are affected also by the proportion of malt adjuncts used, being reduced by such. Roughly it is possible to deduce the proportion of adjuncts from considerations of the original gravity and residual nitrogen, but this always assumes the use of malts of normal nitrogen content (L. J. Smith, J. Inst. Brew. 1926, 32, 220).

The following table shows the range of percentages of certain constituents of beer, the higher figures corresponding to all malt beer. They are approximately true of lager as well as ale.

Original gravity.	Ash.	P_2O_5	Nitrogen.
1,050	0·2–0·3	0·050–0·067	0·04–0·07

As regards content of alcohol and of residual solids the composition of a number of beers is given in the following table, which includes extreme as well as average examples (A. C. Chapman, J. Inst. Brew. 1932, 38, 83):

	Total solids. %	Alcohol, % by weight.	Approximate original gravity.
Mild Ale	2·32	2·92	1032·5
	2·53	2·19	1027·5
	5·17	2·90	1044
	6·00	3·94	1055·5
General	3·7–4·8	3·1–3·3	1042
Bitter and Pale Ale	2·23	2·40	1028
	6·87	3·27	1053·5
	4·63	4·66	1055
General	3·8–4·3	3·6–3·9	1046
Stout and Porter	3·86	2·58	1036
	7·04	3·82	1058·5
	5·78	4·55	1059
General	5·0–5·8	3·45–3·75	1050
Strong and Old Ale	6·72	4·72	1064
	10·42	5·28	1083
	5·15	9·38	1092
Lager (English)	4·89	4·00	1051
Pilsener (German)	4·14	3·55	1045
Pilsener (Danish)	4·45	3·46	1045
Pilsener (Czechoslovakian)	5·60	3·54	1050
Munich	5·55	3·61	1051
American "3·2%"	11·0	3·05	1068

R. H. H.

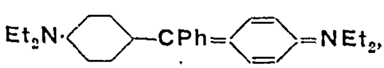
BREWSTERITE *v.* Barium.

BRICKS *v.* Building Materials, Section I.

BRIDELIA BARK or ASDUANA. The bark of *Bridelia montana* is a useful Indian astringent (Dymock, Pharm. J. [iii], 7, 309).

BRILLIANT BLUES *v.* Anthraquinone Dyestuffs.

BRILLIANT GREEN. Tetraethyldiaminotriphenylmethane,



sulphate of a triphenylmethane dyestuff.

BRILLIANT PHOSPHINES *v.* Acridine Dyestuffs.

BRIMSTONE. The old name for sulphur, now used when referring to its inflammable character.

BRITANNIA METAL is an alloy of variable composition, formerly largely used for domestic utensils and generally consisting mainly of tin, with which is alloyed from 5 to 10% antimony and 1 to 3% copper. In the cheaper qualities of this metal small quantities of lead and zinc are also present. Owing to increase in the price of tin, Britannia metal has been largely superseded by nickel silver, an alloy of copper, zinc, and nickel.

BRITISH GUM *v.* ADHESIVES.

BROCHANTITE. A hydrated basic copper sulphate, $CuSO_4 \cdot 3Cu(OH)_2$, forming bright-green orthorhombic crystals, found in Cornwall, Urals, etc. It is largely present in some of the Chilean copper ores. L. J. S.

BROGGERITE. A crystallised variety of the mineral pitchblende or uraninite, found as small, isolated octahedra and cubo-octahedra in the felspar quarries near Moss in Norway. It contains about 80% uranium oxide, together with thorium, lead, etc. *Cleveite* is a very similar, or identical, mineral found in the felspar quarries near Arendal in Norway. L. J. S.

BROMAL. Tribromacetaldehyde, $CBr_3 \cdot CHO$. Prepared by passing bromine into a solution of paraldehyde in ethylacetate (Pinner, Annalen, 1875, 179, 68), or by passing bromine into absolute alcohol, fractionally distilling the product, and treating the fraction boiling at 165°–180° with water. The bromalhydrate thus formed is decomposed on distillation into bromal and water (Schäffer, Ber. 1871, 4, 366; Lowig, Annalen, 1832, 3, 288). Bromal is an oily liquid, b.p. 174°/760 mm.; sp.gr. 3·34. Alkalis decompose it on heating into bromoform and a formate.

Bromalhydrate, $CBr_3 \cdot CH(OH)_2$, crystallises from water in colourless monoclinic prisms containing one molecule of water of crystallisation, m.p. 53·5°. It is less soluble than choral hydrate (Pope, J.C.S. 1899, 75, 460). The fusion and density curves have been determined by Efremov (J. Russ. Phys. Chem. Soc. 1918, 50, 338).

Bromal Alcoholates. Bromalethylalcoholate, $C_2HBr_3O \cdot C_2H_6O$, is a crystalline solid, m.p. 44°; readily soluble in alcohol, sparingly soluble in water (Schäffer, *l.c.*).

The following condensation products of bromal have been prepared: *Bromalammonia* (Schiff and Tassinari, Ber. 1877, 10, 1786); compound with *hexamethylenetetramine* (Lederer, B.P. 17693, 28/7/97; J.S.C.I. 1897, 16, 1039); compounds with *formaldehyde* (Pinner, Ber. 1900, 33, 1432); with *acetaldehyde* (Nakai, Biochem. Z. 1924, 152, 258); *bromaldiacetate* (Gabutti, Gazzetta, 1900, 30, ii, 191); *bromalglycolate* (Gabutti, J.C.S. 1902, 82, i, 261); and *bromalchloralcarbamide*,

$CBr_3 \cdot CH(OH) \cdot NH \cdot CO \cdot NH \cdot CH(OH) \cdot CCl_3$

(Kalle and Co., G.P. 148462; J.C.S. 1902, 82, i, 429). The reaction between bromal and urea has been further investigated by Chattaway and James (Proc. Roy. Soc. 1932, A, 137, 481) and also by Yelburgi (J. Indian Chem. Soc. 1933, 10, 383).

The condensations with hydrazine, benzaldazine, and semicarbazide have been examined by Knöpfer (Monatsh. 1916, 37, 357), who gives details of the products obtained.

BROMBUTOL. *Brometone.* Tribromo-*tert*-butyl alcohol, $CBr_3 \cdot CMe_2 \cdot OH$; crystals, m.p. about 167°, slightly soluble in water, produced by acting on bromoform with acetone. Sedative.

BROMELIA. This synthetic perfume is β-naphthyl ethyl ether, $C_{10}H_7 \cdot OEt$, it has a powerful neroli odour, and is known as *Nerolin II.* It has been—and is sometimes—also known as *fragarol*, although this name is now usually assigned to the corresponding *iso*butyl ether. It has m.p. 36°–37°; b.p. 280°–282°; sp.gr. at 40° 1·0547. E. J. P.

BROMELLITE. A mineral consisting of beryllium oxide, BeO, and named after the Swedish mineralogist Magnus von Bromell (1679–1731). A few minute white crystals have been found in an iron mine at Långban in Sweden. These are hemimorphic hexagonal prisms with the zincite (ZnO) type of crystal structure, and they are pyroelectric. They are remarkable for their high degree of hardness (H. 9), equal to that of corundum and amongst minerals exceeded only by diamond; sp.gr. 3·017. The mineral is insoluble in acids and is not attacked by fused alkali carbonates, but is decomposed by fused $KHSO_4$. Analysis showed 98·02% BeO, with small amounts of CaO, BaO, Al_2O_3, etc. (G. Aminoff, Z. Krist. 1925, 62, 113). L. J. S.

BROMINE. Symbol Br, at. wt. 79·916, at. no. 35, isotopes 79, 81. Bromine is one of the halogens and is the only element other than mercury which is liquid at ordinary temperature and pressure. It was discovered by Ballard in 1826. It derives its name from βρῶμος, a stench.

At ordinary temperatures and pressures bromine is a brownish red liquid with a most irritating smell. It is very volatile, the vapour is yellowish red becoming less transparent when heated. Its boiling point as determined by Pierre, 1847, is 63°; by Andrews, 1848, 58°/760 mm.; by Thorpe 59·27°/751 mm.; by Ramsay and Young 37·65°/749·8 mm., 58·85°/755·8 mm., 58·7°/771·2 mm. Its melting point, by Ramsay and Young, is 7·0–7·47° (J.C.S. 1886, 49, 453).

Liquid bromine has d_4^0 3·18828 (Thorpe); if free from chlorine d_4^{25} 3·10227 (Andrews and Carlton). The coefficient of expansion is 0·0011 between 25° and 30°. The specific heat of solid bromine is 0·08432 g.-cal., of the liquid 0·1071 g.-cal., and of gaseous bromine 0·0555 g.-cal.

The latent heat of evaporation at b.p. is 45·6 g.-cal., the critical temperature is 302·2°. The vapour pressures at various temperatures taken from B. Roozeboom (Rec. Trav. Chim. 1884, 314) and Ramsay and Young (J.C.S. 1886, 49, 453) are:

°C.	mm. Hg.	°C.	mm. Hg.
−80·0	0·13	12·55	119
−59·9	0·79	16·40	139
−41·3	2·89	18·15	152·5
−19·4	16·7	20·6	172
−10·05	35·0	22·65	190
− 7·1	44·5	25·05	212
− 0·13	62	29·8	259
1·8	67·3	34·7	314
4·0	77·3	39·6	378
4·95	82	45·6	478
5·95	86·5	49·8	553
7·90	95	54·7	658
9·95	104	59·5	768

The solubility of bromine in water (Winkler, *Chem.-Ztg.* 1899, **23**, 687) is :

Temp. °C.	1 part Br is dissolved in parts H_2O.	100 parts H_2O dissolve parts Br.	100 parts Br water contain parts Br.
0·00	24	4·167	4·00
10·34	26·74	3·740	3·62
19·96	27·94	3·578	3·46
30·17	29·10	3·437	3·33
40·03	29·02	3·446	3·34
49·85	28·39	3·552	3·41

The solubility of bromine in water is influenced by the presence of chlorine as indicated below :

Cl, g. per litre	5	10	15	20
Br, g. dissolved	46	56	55	54

Salts affect the solubility of bromine in water. The solubility (in g. per litre) with 1 g. mol. of the following salts is :

Na_2SO_4	24	NH_4Cl	82·2
$(NH_4)_2SO_4$	77·7	$NH_4C_2H_3O_2$	340·5
NaCl	55·9	KBr	88·5

The solubility of bromine in the final mother liquors of bromine manufacture is of technical importance :

At	2°	10°	20°	30°	40°	50°	55°
	64·4	64·0	63·6	63·2	60·8	60·0	58·4

g. Br are soluble in 1 litre.

The following table (J. Slessor, J. nat. Phil. Edinb. 1858, [ii], **7**, 289) gives the specific gravity of aqueous solutions of bromine of different concentrations :

Parts Br per litre.	Sp. gr. at 15·6°
10·72	1·00901
11·68	1·00931
12·05	1·00995
12·31	1·01223
19	1·01491
20	1·01807
31·69	1·02367

The vapour pressure of bromine water over liquid bromine is given in the table below (Roozeboom, Rec. trav. chim. 1884, **3**, 75) :

Temp. °C.	mm. Hg.
0·0	68
2·0	76
3·0	80
3·95	83
4·95	88
5·95	92
6·2	93
6·95	96
7·95	101
10·0	110
12·5	124
15·9	146

Bromine water when cooled deposits bromine hydrate in hyacinth-red octahedral crystals. Giran (Compt. rend. 1914, **159**, 246) proposed $Br_2,8H_2O$ on the strength of thermo-chemical and analytical data in the place of the composition $Br_2,10H_2O$ usually given (Löwig, Ann. Phys. Chim. 1829, **16**, 376). The solubility of water in bromine is uncertain ; according to Wildermann 100 mol. Br dissolve 0·4 mol. H_2O.

Bromine is very soluble in alcohol, ether, carbon disulphide, chloroform, carbon tetrachloride, hydrogen chloride, arsenic chloride, sulphuryl chloride and sulphur dioxide. Sulphuric acid dissolves traces only. It is miscible with liquid chlorine and appreciably soluble in compressed gases, particularly oxygen, which at 300 atm. holds six times the quantity with which it is saturated at ordinary atmospheric pressure.

Bromine reacts vigorously with hydrogen, sulphur, phosphorus, arsenic, antimony, tin, aluminium, the heavy metals and potassium ; but it does not react with sodium or magnesium even at 200° (Merz and Weith, Ber. 1873, **6**, 1518). It combines with unsaturated organic compounds and acts as a bleaching agent and disinfectant. Its vapour acts on the mucous membrane and occasions great irritation. Respiration of the vapour causes diminution of red corpuscles and of the content of hæmoglobin in the blood. The extent of diminution increases with the quantity of the vapour administered, but not with repetition of the treatment. Habituation of the animal organism to bromine is attainable by gradual increase in the dose, but when continued, small doses produce hæmolysis (Marino, Arch. Farm. sperim. 1920, **29**, 48).

Bromine crystallises in the orthorhombic system and is isomorphous with chlorine. The crystals are strongly pleochroic, the absorption being dark brownish-red parallel to the principal (prism) axis, yellowish-red parallel to the long lateral axis, and pale yellowish-green parallel to the short lateral axis ; with decreasing temperature the intensity of colour diminishes becoming pale yellow at the temperature of liquid air due to gradual disappearance of pleochroism (Walter Wahl, Proc. Roy. Soc. 1913, A **88**, 348, 313). Bromine is opaque to X-rays ; the degree of opacity of bromine compounds is in direct proportion to their percentage of Br.

Uses.—Before the Great War the principal consumption of bromine was in the manufacture of bromine compounds for use in photography, dyes, and drugs ; for compounds such as bromoform (sp.gr. 2·9), and as a chemical reagent. During the war the consumption increased owing to the use of tear gases. Since the war the production of ethyl bromide in connection with the manufacture of anti-knock compounds for motor-car engines is much greater than the pre-war output.

Occurrences.—Bromine has a wide distribution both in the hydrosphere and in the solid crust. It is never found free and occurs in nature chiefly in combination with alkalis and alkaline earths, also as AgBr, bromargyrite or bromite, as embolite isomorphous with AgCl in Mexico, Chile, Honduras, in some Silesian zinc ores, and in Chile saltpetre. It occurs in sea water and is a constituent of many marine plants and animals. Bromine, as tetrabromindigo, has been found to be secreted by certain species of *Murex*, and is an essential constituent of the Tyrian purple of the ancients. Traces of bromine are occasionally to be met with in coal, and hence in gas liquors. The granite of Fredrikshald contains 2 mg., and the basalt of Daltenberg, near Linz, 8 mg. per kg. ; iron meteorites contain 2·2 mg., stony meteorites

20–26 mg. per kg The springs of Schulz Tarash contain 0–29 mg, and of Val Sinestra 1·35–3 75 mg per litre. In the mineral springs of Germany the bromine varies from a trace to over 100 mg. per kg of water, while those of France contain from a trace to 16 mg per kg. of water.

The important sources which are given here under are in certain hot springs and mineral springs, in sea water and some inland lakes (Report Imp Inst 1928)

British Empire—Bromine is at present only produced from Dead Sea brine within the British Empire, but there exist sources whence supplies of bromine might be obtained if necessary, the Rann of Cutch in India being the most important.

United Kingdom.—Brine from the Point of Ayre, Saltfield, Isle of Man, contains 0·16% of bromine. It occurs in the mineral springs at Woodhall Spa

The Salt Union, Ltd, of Cheshire, pump 500 million gallons of raw brine per year for salt manufacture, this contains 0 08 g. of bromine per litre, and corresponds to a total bromine content of 180 tons The operations of the company are, however, carried on over a scattered area, and under present conditions of production the recovery of the bromine is regarded as commercially impracticable

India.—The brine from manufacture of salt in the Rann of Cutch contains what is considered a workable quantity of bromine, the total of which is stated to amount to 1,800 tons annually.

Wallis found that the bromine content of fresh brine varied from 0–0 025%, while that of the bitterns varied from 0 25–0 5%. Analyses made at the Government Laboratory, London, showed the average bromine content of five brine samples to be 0 06%, and of the three bittern samples, 0 53%. In an actual experiment made on 180 gallons of bittern at the magnesium chloride plant at Kharaghoda, it was found that, after the removal of magnesium chloride and magnesium sulphate by crystallisation, there were 64 gallons of liquor left, which contained 1·18% of bromine. The amount corresponds to 0 4% for the original liquor. Bromine also occurs in the mother-liquors of Chepauk (Madras).

The question of establishing a chemical industry in connection with the salt industry at Kharaghoda, which would probably involve the recovery, amongst other materials, of bromine and potash, has been under consideration.

Palestine.—The following analyses were made in the Government Laboratories, London, from samples taken by Major Brock in 1919, representing the composition of Dead Sea water at various depths:

Composition.

Depth.	Sp gr	KCl	$MgBr_2$	NaCl	$MgCl_2$	$CaCl_2$	$CaSO_4$	Insol	Total salts in grams per litre.
Surface	1·1646	9 96	4·45	70 96	109 50	31 01	1 32	—	227·10
20 ft	1·1756	10 55	5 09	74·57	117 9	33 20	1·45	—	242·76
100 ,,	1·2036	13·21	6 12	80 22	141·72	40 09	0 96	—	282·32
300 ,,	1 2358	15·11	7·24	92 59	170 3	46 95	0 63	—	332 82
360 ,,	1·2343	15 67	7 30	87 38	169 04	46 66	0 64	—	326 69
490 ,,	1·2354	15 89	8 07	87 09	169·21	46 86	0 60	—	327·72
530 ,,	1·2360	15 69	8 00	87 64	169·72	47·16	0 62	—	328 83
1,085 ,,	1·2357	15·54	7 83	85 51	170 66	47·46	0 63	0 32	327·63
1,090 ,,	1·2366	14 95	7·00	93 32	168 9	47·91	0 68	—	333 08

The quantities of salts in the Dead Sea are, therefore, approximately:

Potassium chloride .	2,000	million met. tons.
Magnesium bromide	980	,, ,, ,,
Sodium chloride .	11,000	,, ,, ,,
Magnesium chloride	22,000	,, ,, ,,
Calcium chloride .	6,000	,, ,, ,,

The liquors left after the separation of the carnallite have a sp gr. of 1·34 and consist of about 3 parts of magnesium chloride and 1 part of calcium chloride together with magnesium bromide. The amount of the latter is then about 1·5%. By further solar evaporation during the months of July, August, and September, magnesium chloride can be separated as a network of long crystals which can be easily handled. The liquors after such a separation contain no more bromine, as magnesium bromide crystallises out with magnesium chloride.

Origin.—The origin of the potash and bromine, as well as a considerable portion of the other salts, is doubtless in the hot springs as is indicated by the analysis of the Tiberias hot springs made at the Government Laboratory, London.

	g. per 1,000 g
Calcium carbonate, $CaCO_3$ . . .	0 08
Calcium sulphate, $CaSO_4$ . . .	1 09
Calcium chloride, $CaCl_2$ . . .	8 52
Strontium chloride, $SrCl_2$ . . .	0 15
Magnesium chloride, $MgCl_2$ . . .	2 30
Magnesium bromide, $MgBr_2$ . . .	0 26
Sodium chloride, NaCl . . .	17 03
Potassium chloride, KCl . . .	0 55

Of these salts the concentration of all but the strontium chloride is well known. The volume of the springs discharging at the surface would not account for the amount of potash which is yearly delivered by the Jordan into the Dead Sea, viz. 40,000 tons, for that of the Tiberias springs is less than 400 tons. The

solution of the problem is, however, indicated in analyses which show that the water of the Jordan in passing through the lake becomes charged with salts.

PARTS PER MILLION.

	Galilee incoming water.	Galilee outgoing water.	Jordan. Allenby bridge.
1. Chlorine, Cl	9·6, NaCl 16	240 } NaCl 330	316, NaCl 290
2. Sodium, Na	10·0, $NaHCO_3$ 13	133 }	117
3. Magnesium, Mg	7·8	28·5, $MgCl_2$ 53	62, $MgCl_2$ 185
4. Calcium, Ca	46·0	48	73
5. Sulphate, SO_4	5·6	38	6·3
6. Carbonate, CO_3	60·0	—	165
7. Bromine, Br	not detected in 6 litres	2	3
8. Potassium, K	2·0	7	10

1 to 6, by Irwin; 7 and 8, by Government Analyst, Jerusalem.

FRANCE.—The potash mines of Alsace are the principal source of bromine in France. Mother-liquors utilised in the basin of Mulhouse have the following composition:

KCl	14	per cent.
NaCl	24	,, ,,
$CaSO_4$	2·5	,, ,,
$MgCl_2$	0·12	,, ,,

2·1 g. *bromine per litre.*

There exists still another very abundant source of bromine in certain saline lakes of North Africa and, in particular, in the Sebkha el Melah of Zarzis with a surface of 15,000 hectare.

The mother-liquors of this lake contain:

NaCl	158 g. per litre.
$MgSO_4$	32 ,, ,, ,,
$MgCl_2$	141 ,, ,, ,,
KCl	13 ,, ,, ,,

2·24 g. bromine per litre.

The natural density of the liquors is about 27° Baumé, and they contain as much bromine per cubic metre as 40 cu.m. of sea water.

When they are concentrated to 36·3° Bé by solar evaporation, the content of bromine increases to 8 kg. per cu.m.

Salterns.—The mother-liquors of the salterns of the coast of France, after separation of salt, have a varying composition with an average content of salt as follows:

NaCl	154·24 g. per litre.
KCl	22·12 ,, ,, ,,
$MgCl_2$	112·43 ,, ,, ,,
$MgSO_4$	77·19 ,, ,, ,,
NaBr	2·74 ,, ,, ,,

GERMANY.—The bulk of the world's bromine is produced from the potash deposits of Stassfurt, Germany. These deposits extend over an area 250 miles long and 140 miles wide in the Prussian provinces of Saxony and Hanover. The chief potash salts are carnallite, kainite, and sylvite; the carnallite may contain about 0·20% of bromine. As about 10 million tons of carnallite are mined per year, the amount of bromine is 20,000 tons. Only a small proportion of this is produced, however, owing to the restricted market, there being but a dozen bromine plants amongst 50 or so companies producing potash and operating over 200 potash mines.

The mother-liquor left after the extraction of potash at the potash works contains about 0·25% of bromine in the form of magnesium bromide.

German bromine is sold in three grades: (1) crude, containing 2–5% of chlorine; (2) refined, containing 0·3%; and (3) chemically pure, containing a trace of organic matter but no chlorine.

Composition of mother-liquors.—The composition of mother-liquors utilised in the potash mines of the basin of Stassfurt is apparently the following:

Bitterns called Endlaugen. *d* 1·31.

$MgCl_2$	318 g. per litre.
$MgSO_4$	50 ,, ,, ,,
KCl	14 ,, ,, ,,
NaCl	12 ,, ,, ,,

2–4·5 g. Br per litre in the form of $MgBr_2$.

Bitterns called Urlaugen. *d* 1·25.

$MgCl_2$	236 g. per litre.
$CaCl_2$	116 ,, ,, ,,
KCl	32 ,, ,, ,,
NaCl	9 ,, ,, ,,

3·5 g. Br per litre.

UNITED STATES.—The production of bromine from the bitterns left after salt production has been carried on in the United States since 1846, principally in the States of Michigan, Ohio, and West Virginia. The brines are of comparatively low grade and contain from 0·038–0·180% Ohio, from 0·023–0·139% Michigan. Bitterns produced from ocean water at San Diego, California, contain about 0·2% of bromine, whilst those produced at saltworks in San Francisco Bay contain about 0·35%. The two principal companies are the California Chemical Company and the Dow Chemical Company at Midland, Michigan, which has in recent years produced about three-quarters of the output of bromine in the United States.

Bromine is now produced directly from sea water by the Ethyl Daw Co. Inc. on the long, narrow promontory which separates the Atlantic Ocean from the Fear River, North Carolina. Sea water is pumped from the ocean and discharges

into this river. Various methods were tried, but that finally adopted consists of liberating the bromine with chlorine and blowing out with air. In order to suppress the combination of the elements of water with bromine,

$$3Br_2+3H_2O \rightarrow HBrO_3+5HBr,$$

the hydrogen ion concentration must be increased to a p_H of 3 to 4, which is accomplished by the addition of 0 27 lb of 96% sulphuric acid to one ton of sea water The control with the use of such enormous quantities of water is effected by measurement of the oxidation potentials between a saturated calomel electrode and a platinum electrode With 60 to 70 parts per million of bromine (3 5% total solids in a solution acidified to p_H 3 to 4), the potential rises to 0 88–0 97 volts with the complete liberation of bromine, both p_H and potential being shown by meters The use of aniline as a carrier of bromine

$$3NaBr+3Cl_2+C_6H_5 NH_2 \rightarrow C_6H_2Br_3 NH_2+3NaCl+3HCl,$$

was abandoned, as it involves the use of an expensive raw material and requires twice as much chlorine In each extraction unit after introduction of H_2SO_4 and Cl_2 the sea water is pumped to the top of the blowing out tower, where it passes in sprays down the tower which is filled with wood packing and meets the counter current of air, this carries off the bromine to the absorption tower, where it passes through successive chambers in which a solution of soda ash is circulated in various stages of concentration The reaction is represented by the equation :

$$3Na_2CO_3+3Br_2=5NaBr+NaBrO_3+3CO_2$$

The bromine is then recovered from the salts by the usual methods. The capacity of the plant, which was 7½ short tons per day, is to be increased to 10,000 tons per annum

The bromine is used in the manufacture of ethylene dibromide (L. C. Stewart, Ind Eng Chem 1934, 26, 368)

DEVELOPMENT OF THE BROMINE INDUSTRY IN FRANCE.—Before the war there was but one small factory operating at Pond de Berre in France. Several factories were built during the war both in France and Tunis, but these ceased their manufacture in 1918, save that of Salins-de-Giraud, which continued and was the only one until 1926, when the "Mines Dominiales de Potasse d Alsace" and the "Mines de Kali-Sainte-Thérèse" established factories at Amelie and Ensisheim.

The following details and descriptions of the plant and the process for the recovery of the bromine are taken from a paper by Kaltenbach (Chim. et Ind 1931, 25, 543), who supplied the plant.

The first plant constructed was similar to those started during the war, but the later models show considerable improvements, and they give 3 or 4 times the production of the old type.

The essential feature of the process is the circulation of the liquors between the solution vats and the crystallisation plant, the bromine being removed as a by-product *en route*. As bromine is extracted at each passage the content decreases progressively until a state of equilibrium is reached, when it does not pay to carry the process further. The residual liquor then contains about 2·1 g. per litre, but can be somewhat further reduced in the improved plant. The process is based on the displacement of bromine by gaseous chlorine, which is brought into close contact with the mother-liquors previously heated to a temperature of ebullition. The plant is designed to give continuous working, and each unit consists of a tower made generally of granite in which are perforated stoneware slabs through which the liquors at a temperature of about 75° fall as a spray, while the hot vapours and chlorine injected from near the base are forced upwards. The various plants are designed to bring about intimate contact between the chlorine and the liquor and to effect complete removal of the liberated bromine which is then condensed. In order to effect a gradual ascent of the bromine vapour Kubierschky divided the tower into compartments, steam being injected at the base and chlorine at the third compartment. Communication is provided for the ascending vapours

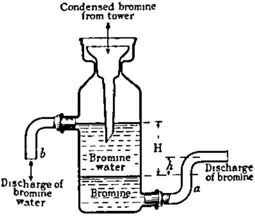


FIG. 1.

by means of vertical pipes passing from the base of each compartment through holes in the perforated plates to the top of the compartment above, through which steam carries the liberated heavier bromine vapour constantly upwards. The descent of the mother-liquors between the compartments is effected by two water sealed valves placed crosswise. The cold liquors obtained from a storage basin are raised to a temperature of about 70°–75° by exchange of heat from the hot exhausted mother-liquors which have a discharge temperature of 107° (Alsace) and 110°–114° (Stassfurt).

Neutralisation of mother-liquors.—The exhausted hot mother-liquors, after leaving the column, traverse first of all a cast iron vessel filled with iron turnings, which fix any bromine carried away in the issuing liquors; these pass into a receptable filled with calcareous stones, the purpose of which is to neutralise any acidity. A fine stream of thiosulphate of soda absorbs the last traces of bromine.

$$Na_2S_2O_3+8Br+5H_2O =Na_2SO_4+8HBr+H_2SO_4$$

The hot liquors are finally discharged into a heat exchanger (economiser) where their heat is

partially absorbed by the fresh mother-liquors which pass through a series of pipes before entering the towers. The bromine vapours, arriving at the top of the column under the chlorine recovery compartment, follow a pipe in the form of a siphon before passing through a serpentine condenser in earthenware from which they fall into a separating bottle.

The liquid bromine mixed with some bromine water leaves the condenser and is collected in a glass Florentine separating bottle. The bromine flows through a lower tube *a*, while the water follows tube *b*, which permits of its return through the chlorine injection tube, and so re-enters the tower (Fig. 1).

It is easy to see that the separating layer

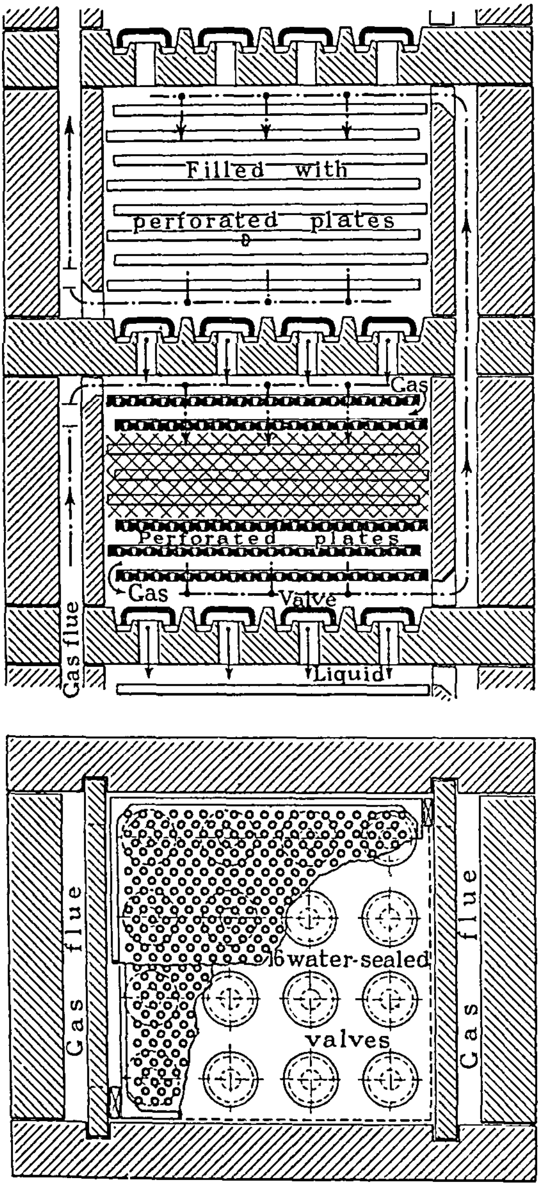


FIG. 2.

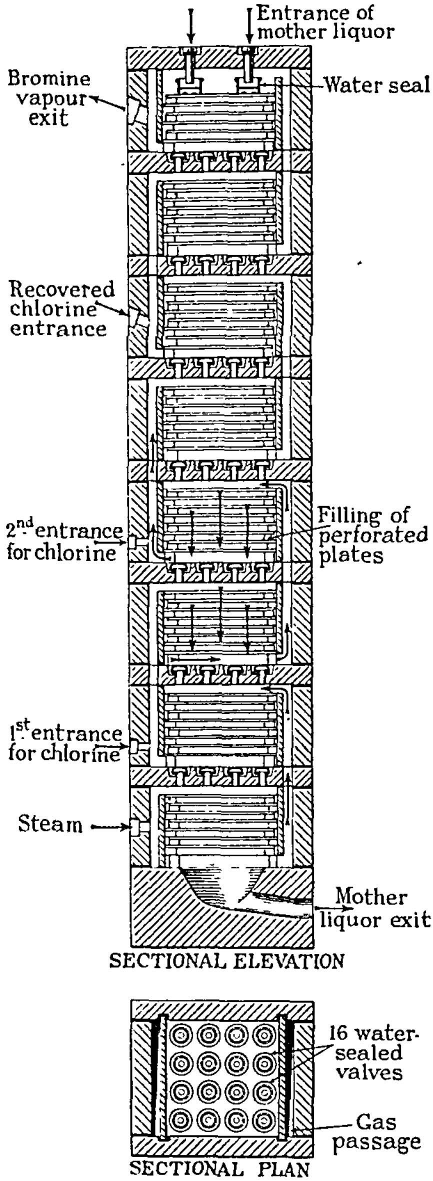


FIG. 3.

between the bromine and water must be at a height:

$$\frac{H}{h}=\frac{D}{d}\;\frac{\text{density of bromine}}{\text{density of the bromine water}}\text{ about } 3:1.$$

Refining of bromine.—The bromine then flows towards a refining apparatus. The operation has for its aim the separation of chlorine by reheating in a sort of dephlegmator. In fact, the chlorine being more volatile than bromine, the vapour contains more chlorine than bromine:

$$5{\cdot}2\,\frac{Cl}{Br}\text{liq.}=\frac{Cl}{Br}\text{vap.}$$

The apparatus consists of a thick leaden or earthenware receptacle filled internally with

Lunge plates of stoneware (perforated earthenware) and heated by a steam-bath. The bromine is heated progressively up to the *temperature of about 55°, which is carefully* controlled. The vapours consisting of a mixture of chlorine, bromine, and chloride of bromine traverse first of all a serpentine stoneware flux condenser which condenses a certain quantity of vaporised bromine, while the mixed vapours containing chlorine are conducted to the upper compartment of the tower where they are absorbed by the entering mother liquors.

The quantity of chlorine injected into the *tower is controlled to an appropriate quantity.* The colour of the bromine water in the separating bottle, which is more or less red, furnishes a fairly precise indication of any great excess of injected chlorine.

The bromine finally traverses a small serpentine lead (or glass) refrigerator, and is

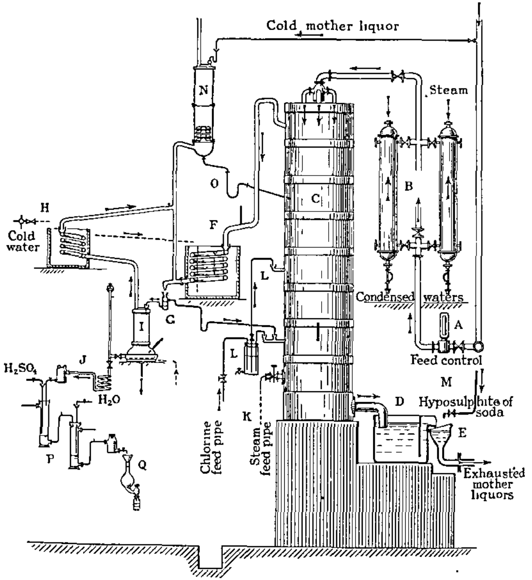


FIG. 4.

then collected in a glass storage bottle from which the bottles of commerce are filled.

Mode of packing.—The bottles into which the bromine is drawn have generally a capacity of 1,200 c.c. and contain 3·75 kg. of pure bromine. They are of glass, of a brown or blue *colour, and are provided* with ground glass stoppers. The packing is done in boxes containing 4 or 6 bottles protected by ash or by kieselguhr.

The above description refers to the type of plant such as was started first in central France, in Tunis and Alsace, and is still common in Germany. The towers comprising the stoneware plates and the outer shell had a total section of 49 sq. dm. and treated about 100 cu m. of mother-liquors in 24 hours.

The extraction of bromine was about 70%.

Recent improvements.—In order to assure an efficacious reaction between two fluids, it is necessary that their contact be also as intimate as possible, a condition obtained by increasing the surfaces of reaction. Permanence of the plant was also required.

In the old type of tower the contact between the liquid and gas was only imperfectly assured, each of them following the path which offers the minimum resistance and opposing each other only in limited zones. On the other hand, the Lunge plates present the unsatisfactory condition of retaining only an insignificant volume of liquid, and the duration of action being therefore very short, reduces to a minimum the reciprocal action of gas and liquid.

In order to remedy these defects the column was modified by Walter and Horst, as shown in

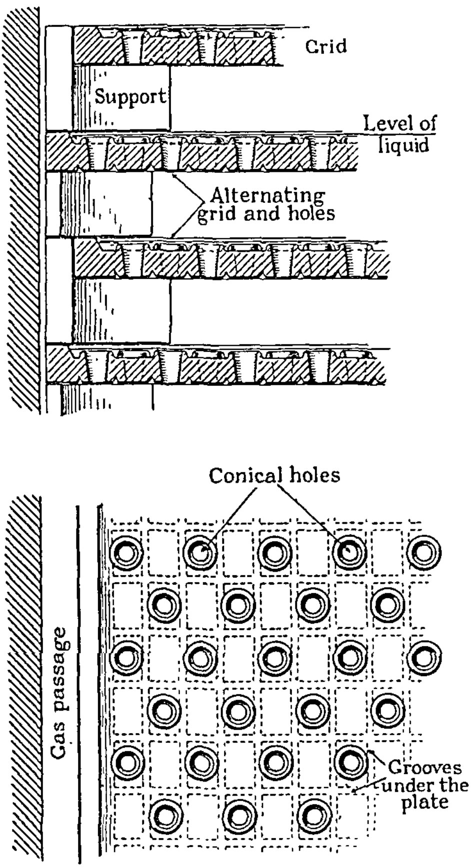


FIG. 5.

Fig. 3, while the general design of the plant is represented by Fig. 4.

The new arrangement of the column forces the gas and the liquids to follow absolutely parallel paths, augmenting thus their reciprocal action and increasing the duration of the action of the vapours.

From Fig. 2 it will be seen that the passage of gas from one compartment to the next in the new plant is made not by tubes but by passages built in the partition wall of the column which extend through the whole breadth, thus ensuring equal pressure and uniform movement of the gas and vapour through the compartments.

On the other hand, the fall of liquid is no more effected by two but by a large number of water-sealed valves in order to assure from the start of the process a uniform distribution of liquor over the whole section.

Finally, the compartment plates are arranged as indicated in Fig. 5, pierced with conical holes surrounded by raised edges, which permit the liquid to remain a certain time on the plate, thus augmenting the duration of the reaction.

The perforations, in consequence of their conical form, help to entangle the vapours with the liquors, an action also assisted by each hole being opposite a plain surface of the lower plate. The progress of the liquid is thus arrested after each fall.

Practical experience has shown plainly the remarkable efficiency of this arrangement, which permits besides to construct columns as large as is desired with the assurance that the efficiency of the plant will be maintained. The new

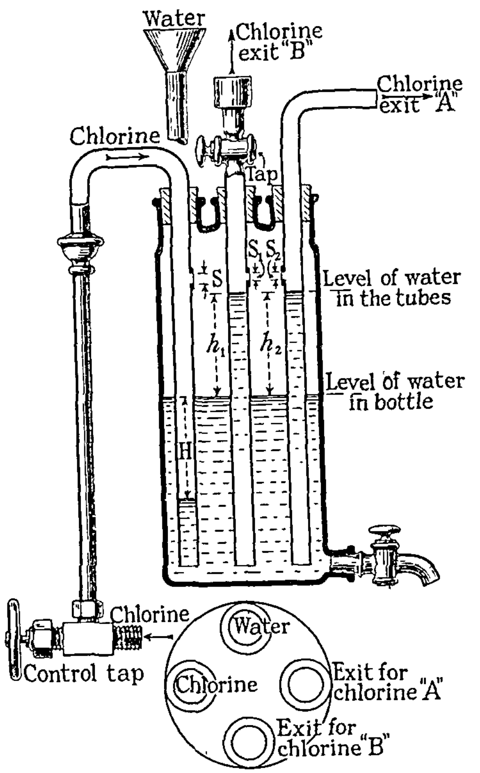


FIG. 6.

columns allow 5 cu. m. per sq. dm. to pass in 24 hours. There is nothing to prevent the construction of towers to treat 600–700 cu.m., and even more, in 24 hours, with the certainty that the results will be equally good.

Working conditions.—Continuous and regular working is indispensable in the plant if it is desired to obtain maximum output; also:

(1) the quantity and temperature of mother-liquors must remain constant during the process;

(2) the volume and the pressure of the chlorine and steam should be maintained constant.

The flow of mother-liquors is regulated by accurate valves, and can also be controlled by flow gauges or measurements of inflow and discharge. Variations in the economisers are

negligible since the temperature of the exhausted mother liquors remains constant

In order to regulate the amount of steam it is advisable to use pressure regulators such as the Arca or Askania type, and thus to maintain the pressure absolutely constant. It is also necessary to see that the regulators remain always in a perfect working condition. This precaution is still more important for regulating the quantity of vapour injected directly into the column, for, when mother liquors poor in bromine are treated, the slightest variation in the quantity of injected vapour can either stop the release of bromine when the pressure drops or cause the passage of the water vapour into the condensation apparatus, which may have disagreeable consequences.

Regulation of chlorine.—For regulating the chlorine a small and extremely simple apparatus represented by Fig. 6 is used, the working of which is very satisfactory.

The gas, the speed of which is regulated by a

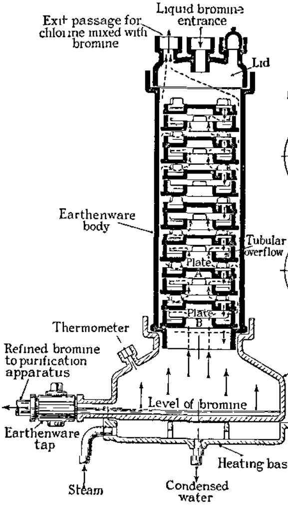


Fig. 7.

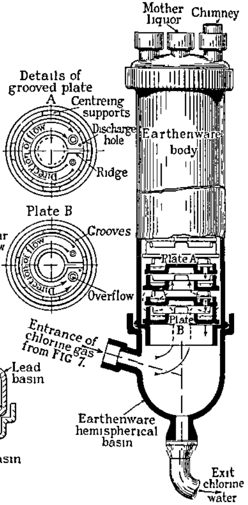


Fig. 8.

needle valve, enters through a tube pierced above the level of the liquid at an appropriate height.

It is readily seen that the supply of chlorine will be given by the formula:

$$V = KS\sqrt{2gh}$$

in which the volume of chlorine V is a function of the section S of the hole multiplied by the root of the height h. It is therefore this height which should be maintained by the workman, to the value which will have been fixed for him in advance.

The distribution of chlorine is uncertain, especially in towers of great capacity, if the gas is all injected through one pipe: to assure therefore the relative value of the partial currents of distribution when a single pipe is employed, it is sufficient to furnish the bottle with the desired number of plunger tubes of distribution, each pierced with a hole of appropriate dimensions corresponding to the partial flow desired. Any lowering of the level in the entrance tube is balanced by an increase in height of the liquid in each of the distributing tubes. The pressure is regulated by introducing water through the funnel, which at the same time governs the flow of chlorine and provides a means of measuring it.

Refining of the bromine.—The old refiners were constituted of thick lead cylinders of 50 cm diameter, fitted internally with a stoneware

plate and placed in basins heated by steam. The volume of liquid bromine amounted to not more than 1 c.c. in a second, and its distribution over a large transverse surface, and consequently its vaporisation, was defective, some of the bromine falling directly to the bottom.

In the new apparatus, Walter reduced the section of the container and altered the shape of the superimposed plates to an annular basin-like form (Figs. 7 and 8), in each of which the bromine is forced to remain a certain length of time, and offers to the vapours as they pass between the successive plates a prolonged contact. The issuing vapours mixed with bromine and chlorine then traverse a serpentine reflux which condenses a part of the bromine, while the chlorine continuing on its way is recuperated by absorption in the mother-liquors.

Whereas in the old type, this absorption is effected in the upper compartment of the tower, in the new type the chlorine absorbing compartment is replaced by a small column (Fig. 8) completely independent and of small diameter and appropriate to the volume of chlorine to be absorbed. The absorption is effected by the cold mother-liquors and the entrance to the column is no longer from above, but through one of the intermediate compartments of the tower below the bromine exit tube. The interior container of the small absorbing column is similar to that of the refiner.

Another very important advantage of this arrangement is that all the vapours issuing from the interior of the tower must traverse the two serpentine condensers, whereas in the old apparatus bromine vapours frequently escaped by the small turret which surmounted the upper compartment.

At the moment when the bromine vapours leave the tower, they are mixed with a certain quantity of gaseous chlorine which is dissolved by the bromine only when the latter is condensed into the liquid form and its temperature diminished to a certain value. In the improved plant, condensation is effected in a serpentine which is cooled just sufficiently to condense the bromine so as to retain only a minimum of chlorine which facilitates the ultimate refining (Fig. 4).

Final purification of the bromine.—The mother-liquors which serve for the manufacture of bromine frequently contain organic matters. When these come into contact with the chlorine in the bromine tower they decompose, giving off complex products such as chloroform as well as carbon dioxide and other gases which disturb the working of the process. In order to eliminate these, the preliminary acidification of the mother-liquors with sulphuric acid has sometimes been recommended, but the remedy is not complete, and the waters thus treated have a troublesome tendency to form foams which also hinder the process. The consumption of chlorine increases greatly with this type of liquor. In practice it rises to 1 kg. or even to 1·1 kg. per kg. of bromine recuperated in the saltern mother-liquors as against a theoretical quantity of 0·445.

With the mother-liquors of Stassfurt the consumption is only 0·58–0·60. Those of Alsace consume about 0·60, but with a perfectly regulated plant it is possible to work to about 0·55. The presence of small quantities of organic matter contained in the bromine liquid itself necessitates final purification. This operation is conducted in an apparatus of continuous working, placed immediately after the refiner, and which is represented by Fig. 9. It consists of two cylinders each supplied with small elements. In the first, the bromine is treated with sulphuric acid of a very high concentration, in the second it is washed by water in order to eliminate the last traces of the enclosed acid. It is thus that the disagreeably valerian odour which manifests itself in the manufactured bromides from the Alsatian bromine is completely eliminated.

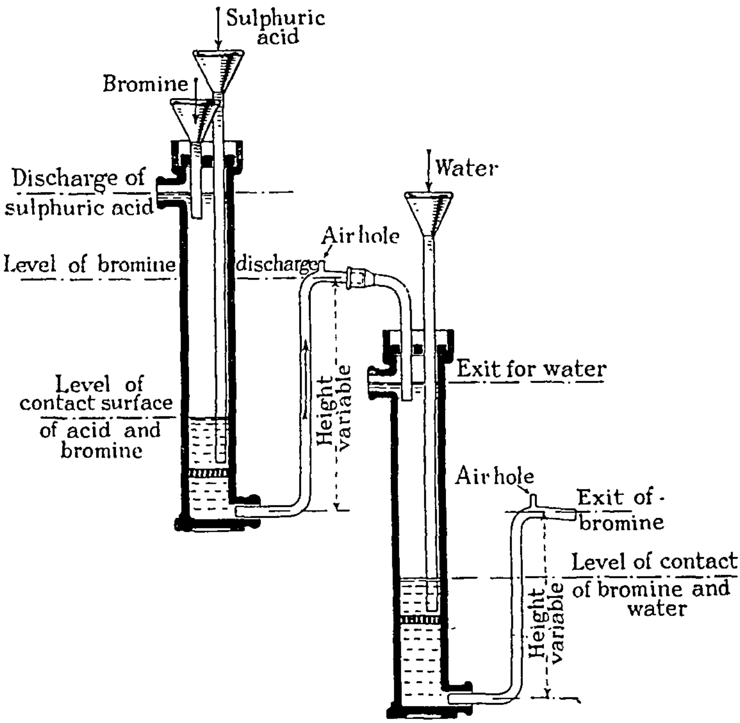


FIG. 9.

The Zarzis mother-liquors which contain only

little organic matter consume about 0 55 of chlorine.

The manufacture of a substance as dangerous as bromine requires particular precautions and watchfulness at every instant. The slightest leak which manifests itself in a joint necessitates repair for fear of rapidly rendering the atmosphere dangerous to respiration. In case of breakage of a receiver containing bromine, ready means of exit for workers and a plentiful supply of fresh air must be available It is desirable also to have a solution of bisulphite of soda at hand.

Fig 10 represents the modern bromine factory equipped with the most recent devices which allows of two towers of great capacity.

PALESTINE —The bromine plant installed by Palestine Potash Limited on the land at the north end of the Dead Sea belongs to the old type. The outside wall of the tower is made of grey granite slabs or blocks which are fitted

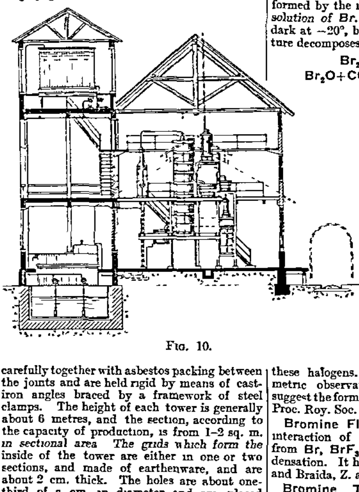


FIG. 10.

carefully together with asbestos packing between the joints and are held rigid by means of cast-iron angles braced by a framework of steel clamps. The height of each tower is generally about 6 metres, and the section, according to the capacity of production, is from 1–2 sq. m. *in sectional area The grids which form the* inside of the tower are either in one or two sections, and made of earthenware, and are about 2 cm. thick. The holes are about one-third of a cm. in diameter and are placed 2 cm apart; consequently, when the liquids descend and the gases and vapours ascend, there is ample opportunity for an intimate mixture. The communicating passages are earthenware pipes in the grid plates, both grid plates and the pipe being of the type referred to on p. 112. The pipes connecting with the condensing apparatus are either of earthenware or of glass, according to the size; the condensing serpentines are of earthenware.

The refiners are of a type similar to the towers, and are made entirely of earthenware, being about three-quarters of a metre in diameter and one metre in height. The outer shell is an earthenware cylinder and, consequently, the inside plates which distribute the vapours and liquors are circular with holes of the grids constructed similarly to those of the tower. In addition to refined bromine, part of the production is converted into iron bromide, for which a special type of plant has been constructed. This is put either in iron kegs or in wooden barrels. For shipment of the bromine the ordinary blue glass bottles are employed. It is perhaps worth noting that the mother liquors from the separation of carnallite contain 1 5% of bromine as against 0 3 or less elsewhere; consequently, the percentage recovery is high.

COMPOUNDS OF BROMINE.

Bromine Oxides.—An oxide, Br_2O, is formed by the interaction of HgO and a CCl_4 *solution of Br. The solution is stable in the* dark at −20°, but in light or at room temperature decomposes :

$$Br_2O \rightarrow Br_2+0\ 5O_2;$$
$$Br_2O+CCl_4 \rightarrow COCl_2+Br_2+Cl_2$$

(Brenschede and Schumacher, Z. physikal. Chem. 1935, B, 29, 356).

An oxide, $(Br_3O_8)n$, has been prepared by treatment of bromine with ozone at −5° to 10° in a closed vessel. The oxide is stable at −80° for several days, it dissolves in water forming an acid solution, titration of which indicates the formula $H_4Br_3O_8$ for the acid (Lewis and Schumacher, Z. anorg. Chem. 1929, 182, 182).

Bromine Chloride.—The fact that a marked diminution takes place in the colour of bromine on mixing with chlorine is a strong argument in favour of the formation of a compound between these halogens. The results of spectro photometric observations on the colour changes suggest the formation of $BrCl$ (Barrat and Stein, Proc. Roy. Soc. 1929, A, 122, 582).

Bromine Fluoride, BrF, prepared by the interaction of Br and F at 10° and purified from Br, BrF_3, and BrF_5 by fractional condensation. It has b.p. 20° and f p. −33° (Ruff and Braida, Z. anorg. Chem. 1933, 214, 81).

Bromine Trifluoride.—Fluorine unites violently with cold bromine vapour (Moissan, Ann. Chim. Phys. 1891, [vi], 24, 240) with production of light but little heat Lebeau (*ibid.* 1906, [viii], 9, 248) showed that the product is bromine trifluoride, BrF_3. It is also produced by the action of fluorine on potassium bromide. BrF_3 is a colourless liquid, m p 8 8°, d^t (liquid) 3 623–0·00277 (273+t), d_4^0 (solid) 3 23 (Ruff, Z. anorg. Chem. 1932, 206, 59) The vapour is strongly irritating and corrosive.

Bromine Pentafluoride, BrF_5, has been prepared by heating BrF_3 with F_2 at 200°; it is a colourless fuming liquid having m.p. −61·3°, b.p. 40·5°, d^t 3·496−0·00346(273+t) (Ruff and Menzel, *ibid.* 1931, 202, 49).

Iodine Monobromide, IBr, is a hard crystalline mass like iodine and has m.p. 36°, it cannot be distilled unchanged, and dissociates even in the solid form (Bornemann, Annalen, 1877, 189, 183; Jos. Hanüs, Z. Nahr.-Genussm. 1901, 4, 1913).

Hydrogen Bromide, HBr, is a colourless, pungent gas of irritating smell. The weight of a litre at normal temperature and pressure is 3·6442 g. It fumes strongly in the air and condenses to a liquid at −73°. It may be obtained synthetically by passing bromine and hydrogen through a heated tube or over heated platinum. It is best prepared by the action of bromine on moistened red phosphorus,

$$5Br+P+4H_2O=H_3PO_4+5HBr;$$

or by the action of a concentrated solution of H_3PO_4 on KBr; or by dropping Br upon melted paraffin heated to 185°.

The gas is very soluble in water and the solution saturated at 0° forms a colourless, strongly acid liquid and contains 68·8% HBr by weight (Roozeboom, Rec. trav. chim. 1885, 4, 102).

If the concentrated acid be heated at ordinary pressures, the gas is evolved until the amount of HBr in the solution sinks to 47–48%, when the liquid boils constantly at 124·3°/760 mm. (Bonner, Bonner, and Gurney, J. Amer. Chem. Soc. 1933, 55, 1409). Such a solution can be prepared as follows: 10 c.c. concentrated sulphuric acid are added to 15 g. of KBr and 0·2 g. $SnCl_2$ in 25 c.c. H_2O. After remaining overnight the clear liquid is decanted from the crystals of $KHSO_4$ which have separated, and distilled, the fraction coming over between 120° and 125° being collected. The yield is more than 90% of the theoretical, and only contains a trace of Cl (Druce, Chem. News, 1923, 126, 1; *see also* "Organic Syntheses," I, 2). This proportion of HBr corresponds to $HBr+5H_2O$, but the liquid is not a true hydrate, since the composition is altered by varying the pressure. The relations between the boiling-point, pressure, density, and concentration of solutions of hydrogen bromide are indicated in the following table (Bonner, Bonner, and Gurney, *l.c.*):

Pressure in mm.	B.p. in °C.	Density at 25°	Comp. in HBr
100	74·12	1·5116	49·80
200	90·35	1·5030	49·28
300	99·91	1·4961	48·83
400	107·00	1·4908	48·47
500	112·94	1·4866	48·19
600	117·82	1·4832	47·95
700	122·00	1·4802	47·74
800	125·79	1·4775	47·56
900	129·13	1·4752	47·40
1,000	132·12	1·4733	47·27
1,100	134·80	1·4716	47·14
1,200	137·34	1·4700	47·03

The density and percentage composition of aqueous solutions of hydrobromic acid are given in the following table (from International Critical Tables, 1928, iii, 55):

%HBr	4	10	20	30
d 20°/4°	1·0269	1·0723	1·1579	1·2580
% HBr	40	50	60	65
d 20°/4°	1·3772	1·5173	1·6787	1·7675

Hypobromous acid may be prepared by the action of bromine water on silver nitrate solution or on silver oxide:

$$Br_2+AgNO_3+H_2O \rightarrow HBrO+AgBr+HNO_3$$

and

$$2Br_2+Ag_2O+H_2O \rightarrow 2HBrO+2AgBr;$$

but the reactions are reversible (Bülmann and Rimbert, Bull. Soc. chim. 1923, [iv], 33, 1465).

Solutions of hypobromous acid, according to Pollak and Doktor (Z. anorg. Chem. 1931, 196, 89), may be prepared by treatment of concentrated silver nitrate solution with bromine and distillation of the filtered solution in a vacuum. If mercuric oxide be used, the mercuric bromide remaining in solution causes reversal of the reaction on heating, whilst silver carbonate reacts but slowly and silver oxide causes decomposition of the acid. The distillate contains also nitric acid, bromine, and hydrobromic acid. The rate of decomposition of hypobromous acid diminishes with time. Of the two probable modes of decomposition, viz.

$$5HBrO \rightarrow HBrO_3+2H_2O+2Br_2$$

and $$4HBrO \rightarrow O_2+2H_2O+2Br_2,$$

the former predominates in the dark at the ordinary temperature; this reaction is bimolecular and appears to be independent of the hydrogen-ion concentration of the solution. Bubbling nitrogen through the solution is without influence. Although bromous acid is a probable intermediate product of the decomposition, it does not appear to be formed in measurable quantity.

Bromic Acid, $HBrO_3$, can be obtained by electrolysis of bromine water or of a solution of HBr or KBr; by warming a solution of perchloric acid with bromine or by the action of bromine on silver bromate suspended in hot water:

$$5AgBrO_3+3Br_2+3H_2O=5AgBr+6HBrO_3$$

The solution thus obtained is a colourless, almost odourless fluid (von Kammer), possessing a sour yet caustic taste (Ballard). The water solution can be concentrated on a water bath with slight decomposition to 4·28% $HBrO_3$, and when this solution is distilled it gives a distillate containing 13·19% $HBrO_3$ or in vacuum a product with 50·59% $HBrO_3$.

Bromine Salt.—In connection with the manufacture of bromine a substance commonly called "bromine salt" is produced which finds application in the extraction of gold ores. It is practically the mixture $NaBrO_3+2NaBr$, and is made by mixing the solid product $NaBrO_3+5NaBr$ (obtained by saturating concentrated caustic soda solution with bromine) with

sodium bromate, electrolytically prepared from bromide, and the mixture finely ground and packed in kegs.

ESTIMATION OF BROMINE IN BRINE AND MOTHER-LIQUORS.

10–50 c.c. of brine acidified with 3 c.c. 6*N*-HCl are titrated in a stoppered bottle with *N*/10 sodium hypochlorite in the presence of acetone. After each addition from the burette the water and acetone mixture is shaken, producing an immediate yellow colour which disappears on continued shaking. The end point is reached when the addition of hypochlorite produces no yellow colour. In this reaction 2 mol. of chlorine correspond to 1 mol. of bromine in the water under test. (1 c.c. *N*/10 hypochlorite = 0·004 g. Br.)

According to Z. Szabo (Z. anal. Chem. 1932, 90, 169), small quantities of bromine can best be determined by treating the solution with 1 g. of $KHCO_3$ and a measured volume of chlorine water (5 mg. Cl_2 per c.c.). The solution is evaporated to dryness and the residue dissolved in H_2O; 5 c.c. of 1% PhOH, 2–5 mg. KI, and 5 c.c. 20% H_2SO_4 are added, and the liberated iodine is titrated with 0·001 *N* $Na_2S_2O_3$. A correction is applied for the amount of Cl_2 used. G. S. B.

BROMINOL. *Brominoleum.* Trade name for brominated vegetable oil. Used in skiagraphy (Abbott, Chicago, Pharmaceutical Products, London).

BROMIPIN, BROMOPIN. A combination of bromine with sesamé oil employed in medicine.

BROMITE or BROMYRITE. Native silver bromide, found in Mexico and in Chile.

BROMOBEHENATE. *Salbromin.* Calcium dibromobehenate (29% Br),

$$(C_{22}H_{41}O_2Br_2)_2Ca.$$

BROMOFORM. *Tribromomethane*, $CHBr_3$. This substance is occasionally met with in the liquid left after the rectification of bromine, in which it occurs associated with *chlorobromoform*, $CHBr_2Cl$ (Dyson, J.C.S. 1883, 43, 46) and *carbon tetrabromide* CBr_4 (Hamilton, *ibid.* 39, 48).

Preparation.—Bromoform may be obtained by mixing 100 c.c. of soda lye, 200 c.c. water, and 20 c.c. bromine. To this yellow solution of hypobromite sufficient acetone (about 10 c.c.) is added to remove the yellow colour and the layer of bromoform which separates is tapped off and rectified. Yield 75% (Denigès, J. Pharm. Chim. 1891, [v], 24, 243). It may also be prepared by the simultaneous action of bromine and caustic potash on alcohol; of bromine and lime on acetone (Beniger, Amer. J. Pharm. 1894, 63, 80); of calcium hypochlorite and potassium bromide on acetone (Fromm, Pharm. Ztg. 1894, 39, 164); and by the action of alkalis on bromal. Electrolytically, it has been made from potassium bromide and alcohol (Fabrik vorm. Schering, G.P. 29771), from potassium bromide and acetone (Coughlin, Amer. Chem. J. 1905, 27, 63; and Muller and Loebe, Z. Elektrochem. 1904, 10, 409); and from calcium bromide, alcohol and water (Trechzinsky, Chem. Zentr. 1907, i, 13). It has also been prepared by the action of bromine on chloroform in the presence of aluminium chloride (U.S.P. 1891415).

Properties.—Pure bromoform is a colourless liquid, d_4^{15} 2·9000, b.p. 146·3°/760 mm., setting-point +7·4° (Buhmann, Arch. Pharm. 1928, 266, 123). Dolezalek and Schulze (Z. physikal. Chem. 1921, 98, 395) assert that the liquid at 25° is associated into bimolecules to the extent of 65%. It is decomposed by potash into potassium bromide, water, and carbon monoxide, and may be estimated by means of this decomposition (Desgrez, Compt. rend. 1897, 125, 780; and Richaud, J. Pharm. Chim. 1899, [vi], 5, 232). Under the influence of light and air it decomposes, the decomposition products depending on the time of exposure and the amount of available oxygen (Schoorl and van den Berg, Chem. Zentr. 1906, i, 441). It has been shown by Tseng (Nat. Centr. Univ. Sci. Rep. 1931, A, 1, No. 2, 1) that bromoform does not react with magnesium in ether. Numerous molar addition products have been described (Steinkopf and Bessaritsch, J. pr. Chem. 1925, 109, 230; 1930, 127, 337; Weissenberger *et al.*, Monatsh. 1926, 46, 281; Sachs and Balassa, Z. anorg. Chem. 1926, 152, 180). It has been used to a slight extent as an anæsthetic, in the treatment of diphtheria, and in cases of whooping cough.

It has been shown to be a more efficient germicide than chloroform (Kudicke and Weise, Arch. Schiffs. Tropen Hyg. 1926, 30, 231).

BROMOPHIN. *Euporphin.* Apomorphine methyl bromide.

BROMOPRENE *v.* BUTADIENES AND POLYOLEFINS (conjugated).

BROMOSTYROL (α-BROMOSTYRENE). This largely used synthetic perfume is also known as artificial hyacinthin, is of a powerful but somewhat coarse hyacinth odour. It is the α-bromophenylethylene, the β isomer is prepared but is not much used in perfumery. Fine hyacinth perfumes are made with phenylacetaldehyde rather than with bromostyrol. Bromostyrol is used in the cheaper types of narcissus, jonquil and hyacinth perfumes. Formula, $C_6H_5\,CH{:}CHBr$; b.p. 221°; sp. gr. 1·425; ref. index, 1·6030. E. J. P.

BROMSULPHALEIN. Disodium phenoltetrabromphthalein sulphonate,

$$O\,CO\,C_6H_4\,C[C_6H_3(OH)SO_3Na]_2$$

A white crystalline powder, containing 37% of bromine; soluble in water, insoluble in alcohol or acetone. Liver function diagnosis.

BROMURAL. Trade name for a *a mono bromisovalerylurea.* Employed as a hypnotic. Forms white needles, slightly bitter in taste; readily soluble in hot water, alcohol, and ether, sparingly soluble in cold water; m.p. 147°.

BRÖNNER'S ACID, 2-naphthylamine-6-sulphonic acid.

BRONZE POWDERS. These are also known as gold powders, and consist of alloys produced in a fine state of division, used in decorative work in various industries. They vary considerably in composition, and generally consist of brasses rather than bronzes, their usual composition lying between 70–85%

copper and 30–15% zinc; small quantities of tin, lead, antimony, arsenic, iron, bismuth, and aluminium are frequently also present.

BROOKITE. A crystalline form of titanium oxide.

BROSIMUM GALACTODENDRON (Fam. Moraceæ). (Cow-tree, milk-tree.) The milky juice is much used in S. America as a substitute for cream. The dried material contains "gutta" 5·5% and resin 83·2%. This could be used as a substitute for pontianic in the rubber industry (Bull. Imp. Inst. 1919, **17**, 294).

BROUSSONETIA PAPYRIFERA (Vent.). *The Paper mulberry.* The fibrous bark is used in China and Japan for the manufacture of a kind of paper, and in Polynesia in the manufacture of Tapa cloth.

BROVALOL. *Bornyl α-bromo*iso*valerate.* A colourless, oily liquid, soluble in alcohol, chloroform, ether; insoluble in water. Sedative.

BROWN ACID (Brown oil of vitriol, B.O.V.). Crude sulphuric acid, sp.gr. about 1·72, containing about 80% H_2SO_4.

BROWN BERRIES. The fruit of *Rubus fruticosus.*

BROWN, CALEDONIAN. Mineral pigment composed chiefly of manganese and iron oxides and hydroxides.

BROWN CAPPAGH. Highly manganiferous and ferruginous earth obtained from the Cappagh mine in Ireland. Used as a pigment.

BROWN, VANDYKE. A bituminous ferruginous earth used as a pigment.

BROWN B. (*Cibanone Yellow R*) *v.* ANTHRAQUINONE DYESTUFFS.

BROWN G.R.B.R. (*Indanthrene Orange 6 RTK*) *v.* ANTHRAQUINONE DYESTUFFS.

BROWN R. (*Caledon Olive R*) *v.* ANTHRAQUINONE DYESTUFFS.

BRUCINE. One of the chief constituents of *Nux vomica.*

BRUCITE. Native magnesium hydroxide, $Mg(OH)_2$, found as platy crystals with perfect micaceous cleavage, or as lamellar masses, in serpentine rocks, at Unst, one of the Shetland Isles, at Texas in Pennsylvania, etc. It sometimes contains a small amount of iron (*ferrobrucite*) or manganese (*manganbrucite*). A fibrous variety is called *nemalite.* L. J. S.

BRUNNER'S SALT. A double sulphide of mercury and potassium, $HgS{\cdot}K_2S,5H_2O$, prepared by dissolving vermilion in a solution of potassium monosulphide.

BRUNSWICK BLACK is prepared by fusing 2 lb. of asphalt and mixing thoroughly with 1 pint of hot boiled oil. When cool, 2 pints of turpentine are added to the mixture. An inferior but cheaper black may be made by boiling gently together for five hours 25 lb. each of black pitch and gas tar asphaltum; 8 gallons of linseed oil, and 10 lb. each of litharge and red lead are then mixed in, and the whole boiled. After cooling, the mixture is thinned by the addition of 20 gallons of turpentine (*v.* also BONE OIL).

BRUNSWICK GREEN. An oxychloride of copper, used as a pigment. Copper filings or turnings are moistened with a solution of sal-ammoniac, and left in contact with the air; the oxychloride so formed is washed off with water, and dried at a gentle heat. The term is, however, usually applied to a mixture of chrome yellow and Prussian blue.

BRUSHITE. A hydrated phosphate of lime, $HCaPO_4,2H_2O$, occurring in the guano of Aves Island and Sombrero in the Caribbean Sea.

BRUSSELS SPROUTS. A cabbage variety (*Brassica oleracea*) in which numerous small heads are developed along a main stalk. The edible portion contains, according to American analyses:

Water.	Protein.	Fat.	Carbohydrates.	Ash.
88·2	4·7	1·1	4·3	1·7

The leaves contain a wax shown by Sahai and Chibnall (Biochem. J. 1932, **26**, 403) to contain *n*-nonacosane, 15-nonacosanone, 15-nonacosanol, ceryl alcohol, cerotic acid, and probably *n*-hentriacontane. A. G. Po.

BRYOIDIN, $C_{21}H_{42}O_3$. A crystalline constituent of *Manilla elemi,* m.p. 135·5°.

BRYONY ROOT was employed from early times for its cathartic properties but has gradually fallen into disuse. The plants yielding the root are *Bryonia alba* and *B. dioica,* the latter being designated as English bryony (English mandrake). The roots of *B. dioica* contain a number of enzymes, including amylase, invertase, and peroxydase (Girardet, J. Pharm. Chim. 1924, [vii], **30**, 75). Several investigations have been carried out on the roots (Silber, Dissertation, Erlangen, 1894; Power and Moore, J.C.S. 1911, **99**, 937; Zellner *et al.*, Arch. Pharm. 1927, **265**, 27; Chaze, Compt. rend. 1932, **195**, 825; Angeletti and Ponte, Gazzetta, 1934, **64**, 569) but without any marked success. Among the many substances isolated may be mentioned an alkaloid-like principle, a glucoside, *bryonin,* $C_{48}H_{66}O_{18}$, which gives rise to glucose and an aglucone, *bryogenin,* $C_{30}H_{46}O_6$; a sterol, m.p. 159°; an alcohol, *bryonol,* $C_{22}H_{34}O_2(OH)_2$, m.p. 210°–212°; a mixture of fatty acids, containing oleic, linoleic, palmitic and stearic acids; and two isomeric substances *α-bryon,* m.p. 300°–301°, and *β-bryon,* m.p. 292°–293°. The activity of the root cannot, however, be attributed to any one of these substances.

BUCHU or BUCCO. The leaves of three varieties of *Barosma* (ord. Rutaceæ), viz. *B. betulina* Bartl et Wendl. f., *B. crenulata* Hook., and *B. serratifolia* Willd., are known under this name. The leaves are used medicinally by the South African natives.

Their composition has been studied by Brandes (Arch. d. N. Apoth. Ver. **22**, 229), Landerer (Buchner's Répert. **84**, 63), Flückiger (Pharm. J. 1874, [iii], **4**, 689; 1881, [iii], **11**, 219), Wayne (*ibid.* 1876, [iii], **6**, 723). By extracting the leaves with light petroleum, Bialobrzeski (Chem. Zentr. 1896, ii, 551) obtained chlorophyll, a resin, and an ethereal oil containing chiefly diosphenol, together with a terpene $C_{10}H_{18}$, b.p. 174°–176°, and a ketone isomeric with menthone, and having the constitution $C_{10}H_{18}O$, b.p. 206°–209°; it yields an oxime and a tribromo-derivative. After extraction with light petroleum, the leaves, on treatment with cold alcohol, yield 3% of a brownish-green bitter resin in-

soluble in benzene, and when the alcoholic extract is treated with sodium carbonate or by other methods diosmin is deposited, forming tasteless, odourless crystals, m p 244°.

According to Kondakoff and Bochtschiew (J. pr. Chem. 1901 [ii], 63, 49), the best oil of bucco or buchu leaves contains 10% of hydrocarbons, consisting of a variety of *d* limonene and dipentene; 60% of a ketone $C_{10}H_{18}O$, $[\alpha]_D$, −16° 6′, b p 208 5°–209 5°, which, on reduction, yields a menthol not identical with the natural product, 20% of dios phenol (*q v*); 5% of resin, and 5% of other constituents (Kondakoff, J pr. Chem 1896, [ii], 54, 433) After removing diosphenol from the oil of buchu leaves, Tschugaeff succeeded in obtaining xanthogenide derivatives of *d* menthol from a fraction of the residue (J Russ Phys Chem Soc. 1910, 42, 714, Skorortsoff, *ibid* ii, 55)

BUCHU, ESSENTIAL OIL OF. The oil distilled from various species of *Barosma*, *B betulina* Thunb, *B crenulata* Thunb, and *B. serratifolia* Willd (Fam Rutaceæ) These shrubs are indigenous to the south west mountainous regions of the Cape of Good Hope. Yield 0 8–2 5% Characters sp gr 918–970, optical rotation −12° to −36°, n_D 1 474–1 486 The oil from *B. betulina* deposits a crystalline mass of diosphenol; the oils from the other two species contain less diosphenol and remain liquid.

Constituents: *d*-limonene, dipentene, *l*-menthone, and diosphenol. The latter is also known as *buchu camphor* and when recrystallised has m p. 83°–84°. Its alcoholic solution gives a green colour with ferric chloride, reduces ammoniacal solution of silver nitrate, and restores the red colour to decolourised fuchsine solution. It gives an oxime but no semi carbazone. It has the properties of a ketone-phenol C. T. B.

BUCKTHORN is the fruit of *Rhamnus catharticus* Linn. (Fam. Rhamnaceæ); it contains dextrose, emodin, emodinanthranol, rhamnoxanthol, jesterin, rhamnocathartin, rhamnetin, xanthorhamnin, and quercetin. The juice is used as a laxative in veterinary practice (B.P.C. 1934).

BUCKWHEAT (*Fagopyrum esculentum*). The seed is grown as a poultry food or for cattle and in America is milled for flour used in preparing buckwheat cakes. Kellner records analyses of buckwheat and its milling offals:

	Water	Protein.	Fat	Carbo-hydrates	Fibre	Ash
Seed	14 1	11·3	2 6	54 8	14 4	2 8
Fine meal	14 7	8 6	1 9	72 6	0 8	1 4
Coarse meal	12 0	31 8	8 4	38 3	4 8	4 7
Fine bran	12 0	15 2	4 5	50 0	11 3	7 0
Coarse bran	15 6	8 0	1 8	34 2	37 6	2 8
Husks	13 2	4 6	1 1	35 4	43 5	2 2
Straw	16 0	4 8	1·2	34 6	38 2	5 2
Whole plant in flower	83 7	2 5	0 6	7 8	4 3	1·1
Whole plant as hay	14 0	10 5	2 1	35 6	31 4	6 4

American data are given by Coe (U.S. Dept. Agric Circ. 1931, No. 190).

The carbohydrate material consists largely of starch, the grains of which have a characteristic shape.

The nitrogen distribution in buckwheat is shown by Hara (Imp Japan Inst. Nutrition, Bull soc hyg. aliment. 1927, 15, 481, 524) to be as follows: amino- 8 2, humin 7 6, cystine 1 8, arginine 23 8, histidine 2 4, lysine 3 2, monoamino 40 5, and non amino- 13 6%. Johns and Chernoff (J. Biol Chem 1918, 34, 439) separated the globulins which had the following partition values: arginine 13, histidine 0 6, lysine 7 9, and cystine 1%. Small amounts of tryptophan were detected.

Parisi and Cosmo (Ital Agric. 1930, No. 5) find the colouring matter of buckwheat to contain a red anthocyanin, the chromogen of which is a yellow powder and yields galactose on hydrolysis. A. G. Po

BUFAGIN, $C_{29}H_{38}O_7$, m p. 220°–221°, a toad venom.

BUFFER SOLUTIONS. The "acidity" of a solution originally referred to its taste, but it is now used synonymously for the hydrogen ion concentration, and R. Dietzel (Kolloid Z 1926, 40, 240) has shown that the reaction on the tongue is indeed proportional to the hydrogen ion concentration. In the case of strong solutions of acids and alkalis the acidity or alkalinity will be proportional to the concentration and will not be very much changed by the addition of small amounts of foreign material Once the hydrogen ion concentration has been determined for a given dilution a similar solution can be made up by the methods of volumetric analysis. In solutions that are nearly neutral the concentration of acid or alkali is very small indeed, and impurities may then have a large effect, as carbon dioxide can be taken up from the air and alkali from a glass container. Such impurities cannot easily be eliminated, and it is better to devise solutions where the hydrogen ion concentration changes as slowly as possible compared with the amount of acid or alkali added. These liquids, that have a reserve of acidity or alkalinity, are known as buffer solutions (E. W. Washburn, J. Amer. Chem. Soc. 1908, 30, 31). Once standardised they are readily made up, and can be used to measure the hydrogen ion concentration of other solutions if the colour of an indicator in the two solutions is compared in a suitable apparatus, "Comparator."

In any aqueous solution the concentration of the hydrogen ion (H^+) multiplied by that of the hydroxyl ion (OH') is a constant K_w, known as the ionic product for water. At 22°C. the value of K_w is 1×10^{-14} if (H^+) and (OH') are expressed in g.mols./litre. In a neutral solution the concentrations of hydrogen and hydroxyl ion must be equal, *i.e.* $(H^+)=(OH')=\sqrt{K_w}=10^{-7}$ g.mols./litre. A convenient scale with which to measure hydrogen ion concentration was introduced by Sørensen who defined the p_H unit as:

$$\log\frac{1}{(H^+)}=-\log(H^+)=p_H$$

Thus the normal range of acidity to alkalinity is covered on a scale of 1 to 14, the p_H of a neutral solution being very close to 7, at 22°C., but changing slightly with the temperature. The dissociation of a weak acid HAc can be calculated with fair accuracy if mass action conceptions be applied to the equilibrium

$$HAc \rightleftharpoons H^+ + Ac'.$$

If the concentrations of the three molecular species be represented by (H^+), (Ac'), and (HAc), we have according to the Ostwald dilution law,

$$\frac{(H^+)(Ac')}{(HAc)}=K_a.$$

For acetic acid $K_a=1{\cdot}8\times10^{-5}$, and consequently with reasonably strong solutions almost all the acid will be present as undissociated molecules. A solution of its alkali salt, on the other hand, is a strong electrolyte, and would be completely dissociated into metal and acetate ions. A solution of a weak acid and one of its alkali salts is a typical buffer solution, and its p_H can be calculated approximately from the concentrations of acid and salt and the value of K_a for the acid. We have seen that:

$$K_a=\frac{(H^+)(Ac')}{(HAc)}$$

Rearranging, $$\frac{1}{(H^+)}=\frac{(Ac')}{(HAc)K_a},$$

taking logarithms,

$$p_H=\log\frac{(Ac')}{(HAc)}-\log K_a.$$

As a further approximation we may put

(Ac')=gross concentration of salt;
(HAc)=gross concentration of acid.

Therefore,

$$p_H=\log\frac{\text{concentration of salt}}{\text{concentration of acid}}-\log K_a.$$

Since the above calculation is based on the Ostwald dilution law it will break down when that law is invalid. More accurate calculations have been made on the basis of the Debye-Hückel theory of electrolytes by C. Morton (Trans. Faraday Soc. 1928, **24**, 14), E. J. Cohn (J. Amer. Chem. Soc. 1927, **49**, 173), and I. M. Kolthoff (Biochem. Z. 1928, **195**, 238). The above treatment applies equally to a buffer on the alkaline side which would consist of a weak base mixed with a salt of that base with a strong acid.

The expression deduced indicates that the p_H of a buffer solution depends solely on the relative amounts of the chemicals present and that there should be no change on dilution. Actually there are small variations with the actual concentrations, as shown by I. M. Kolthoff (*l.c.*) for the p_H of solutions containing equimolecular proportions of acetic acid and sodium acetate.

Normality	*N*/10	*N*/20	*N*/40	*N*/100	*N*/200	*N*/400
p_H . .	4·61	4·63	4·65	4·68	4·69	4·70

He obtained similar variations with other buffer solutions and showed that all of them could be calculated to within a few hundredths of a p_H unit on the basis of the Debye-Hückel theory of electrolytes.

Variations in the p_H value would be expected as the temperature changed owing to the known variations in K_a and K_w. With many buffers these variations are small compared with other errors. Thus L. E. Walbum (Biochem. Z. 1920, **107**, 219) reported that the effect was negligible with the solutions recommended by Sørensen; a similar result was found by I. M. Kolthoff and F. Tekelenburg (Rec. trav. chim. 1927, **46**, 33) except in the case of glycine sodium hydroxide mixtures. That there can be appreciable changes introduced by temperature fluctuations is shown by the work of S. W. Brujevicz and N. P. Karpova (Biochem. Z. 1932, **251**, 60) who measured the p_H of buffer solutions in common use at three temperatures. Some of their results are given in the table below, which shows the changes in p_H of several buffer solutions at three temperatures.

	t= 0°C.	18°C.	25°C.
McIlvaine's citric acid-sodium phosphate buffer	3·087 4·104 5·084	3·031 4·045 5·037	3·025 4·031 5·034
Sorensen's mixed phosphate buffer .	6·135 7·056	6·031 6·969	6·008 6·947
S. Palitzsch's borax-boric acid buffer	7·757	7·710	7·686
Sorensen's borax-sodium hydroxide buffer	10·401	9·929	9·846

In the neighbourhood of room temperature the deviation is generally not large, but there is no doubt that care should be taken in controlling the temperature during measurements involving the use of buffers.

The p_H of buffer solutions may also be considerably changed by the presence of materials that are not themselves acid or alkaline, *e g* certain salts and proteins. Haynes (Biochem Z 1921, 15, 440) showed that the p_H of phosphate and acetate buffer solutions was lowered when any of the chlorides of the alkalis or alkaline earths were mixed with them. J B O'Sullivan (Trans Faraday Soc 1928, 24, 298) obtained even larger changes with other salts of nickel and aluminium. Thus a 0·85 nickel sulphate solution and 0·2 molar acetic acid sodium acetate buffer each had a p_H value of 5·0, but after mixing this had dropped to 4·4. The formation of complex salts may also cause considerable deviations. Thus Kolthoff (Biochem Z. 1928, 195, 238) has shown that citric acid will link with organic compounds containing hydroxyl groups (*see also* L Michaelis, Biochem Z 1931, 234, 139).

The most important practical use of buffer *solutions is to provide a series of standards with which the colour of a suitable indicator in these* solutions and in a solution of unknown p_H may be compared. A variety of mixtures is available for this purpose, and only the more important ones will be dealt with here. Whatever mixture is chosen it is essential that very pure chemicals and water be employed in making it up. The first series of buffer solutions for a p_H range of 1–10 was devised by Sørensen (Biochem Z 1909, 21, 131, 22, 352, Ergebn Physiol 1912, 12, 393). This has been widely used together with the excellent sodium acetate acetic acid mixtures due to G S Walpole (J.C S 1914, 105, 2501, 2521). The boric acid-borax mixtures of S Palitzsch are also well known (Biochem Z 1915, 70, 333) and the disodium hydrogen phosphate citric acid series introduced by T. C. McIlvaine (J. Biol Chem. 1921, 49, 183). This last buffer is easy to prepare and covers a wide range. K. H. Slotta and W. Franke (Ber 1931, 64, [B], 452) have redetermined the values obtained when a 0·2 molar solution of secondary sodium phosphate is mixed with a 0·1 molar solution of citric acid. Since the buffer is a useful one their results are given in the table below

c c of 0·2 molar Na_2HPO_4	c c 0·1 molar citric acid	p_H of resulting mixture
0·79	4·21	2·88
1·24	3·76	3·20
1·61	3·39	3·57
1·93	3·07	3·92
2·21	2·97	4·27
2·47	2·53	4·66
2·68	2·32	5·01
2·90	2·10	5·43
3·16	1·84	5·88
3·55	1·45	6·42
4·12	0·88	6·97
4·61	0·39	7·49
4·86	0·14	8·00

A simple new series of buffer solutions with a constant electrolyte content and covering the p_H range of 1·5–11 has been devised by A. Thiel, G Schulz, and G. Coch (Z Electrochem 1934, 40, 150) (*v infra*). It will be seen that all the solutions can be made by weighing out the appropriate salts

Solution 1 is 0·05 molar with respect to oxalic acid, and 0·20 molar with respect to boric acid

Solution 2 is 0·20 molar with respect to boric acid, 0·05 molar with respect to sodium sulphate, and 0·05 molar with respect to succinic acid

Solution 3 is 0·05 molar with respect to borax.

Solution 4 is 0·05 molar with respect to sodium carbonate.

The p_H values of the solutions obtained on mixing are shown in the following table

p_H of mixture	Solution 1 c c	Solution 2 c c	Solution 3 c c	Solution 4. c.c.
1·5	84·1	15·9		
2·0	34·3	65·7		
2·5	10·0	90·0		
3·0		98·0	2·0	
3·5		89·8$_5$	10·1$_5$	
4·0		79·2	20·8	
4·5		69·1	30·9	
5·0		60·8$_5$	39·1$_5$	
5·5		55·2	44·8	
6·0		51·7$_5$	48·2$_5$	
6·5		46·7$_8$	50·2$_2$	
7·0		47·6	52·4	
7·5		43·4	56·8	
8·0		35·9	64·1	
8·5		24·4	75·6	
9·0		8·3	91·7	
9·5			54·6	45·4
10·0			25·3	74·7
10·5			11·0	89·0
11·0			3·0	*97·0*

Other buffer solutions of importance are succinic acid—borax p_H 3–5·8, and succinic acid—potassium dihydrogen phosphate p_H 5·8–9·2 (I. M. Kolthoff, J. Biol. Chem. 1925, **63**, 135); potassium citrate—hydrochloric acid p_H 2·2–3·6 (I. M. Kolthoff and J. J. Vleeschhouwer, Chem. Weekblad. 1926, **23**, 510; 1927, **24**, 78); disodium hydrogen phosphate-sodium hydroxide p_H 11–12, and sodium carbonate-borax p_H 9–11 (*ibid. idem.* 1927, **24**, 526); sodium acetate-veronal p_H 2·62–9·64 (L. Michaelis, Biochem. Z. 1931, **234**, 139); phenyl acetic acid and its sodium salt p_H 3·2–4·7 (W. L. German and A. I. Vogel, J.C.S. 1935, 912).

E. B. R. Prideaux and Ward (J.C.S. 1924, **125**, 426) introduced a solution in which the p_H changed regularly with the amount of caustic soda added between p_H 3 and 11. On account of this property the mixture was termed a "Universal Buffer Mixture." H. T. S. Britton and R. A. Robinson (J.C.S. 1931, 1456) found that errors of as much as 0·2 of a p_H unit were possible when the above buffer was used and they suggested a modified mixture which may now be purchased ready for immediate use. It is seldom, however, that it is necessary to work over such a wide p_H range and consequently the "universal mixtures" are normally no more convenient than a simple buffer solution.

Many physiological processes can only occur within narrow p_H limits and the control of p_H is of vital importance in the animal body. The blood normally has p_H between 7·3 and 7·4 and has considerable buffer power owing to the presence of alkali hydrogen carbonate and carbonic acid. During violent exercise the CO_2 accumulates and the p_H falls somewhat, but the subsequent panting leads to rapid removal of CO_2 through the lungs, and the blood stream may then be temporarily on the alkaline side. In certain types of disease the alkali bicarbonate is attacked by the acids produced in the system, the buffering action of the blood falls off and a condition of acidosis intervenes. In such cases the p_H of the blood may drop below 7·0. Any severe abnormality as, for example, surgical anæsthesia and traumatic shock, will produce changes in the p_H and the alkali reserve of the blood, but the precise significance of these changes is not clear and for further information the bibliography should be consulted.

Bibliography.—H. T. S. Britton, "Hydrogen Ions," Chapman and Hall; W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore; F. D. Snell, "Colorimetric Analysis," Chapman and Hall; J. H. Austin and G. E. Cullen, "Hydrogen Ion Concentration of the Blood in Health and Disease," Williams and Wilkins; C. Lovatt Evans, "Recent Advances in Physiology," Chap. V, J. and A. Churchill. R. H. P.

BUILDING MATERIALS.—There are a number of natural and artificial materials, which, for the sake of convenience, may be grouped under the general heading Building Materials; not that their use is restricted to building or engineering work, but because here they find a major, if not their principal, application. A sub-division of building products into "traditional" and "modern" materials may be attempted, but the division is by no means rigid. Bricks, lime, and natural stones would fall into the former class; Portland cement and some gypsum plasters into the latter. Many of the traditional materials have been markedly improved or modified in recent times and in both traditional and modern products the activities of the technician are involved either in production or the testing of finished products, or both. Amongst recent developments may be mentioned the production of lime in the form of dry hydrates, the use of tunnel kilns in brick manufacture, the introduction of aluminous cement. These features will be referred to in the individual sections which follow.

The present section on Building Materials comprises the following articles:

I. Bricks and Clay Products.
II. Calcium Sulphate Plasters and Cements.
III. Lime.
IV. Magnesium Oxychloride Cement.
V. Natural Stones.
VI. Portland and other Hydraulic Cements and Concretes.
VII. Sand-lime Bricks.

(Asphalt and Bitumen are dealt with in a separate article, Vol. I, 516–517).

F. L. B.

I. Bricks and Clay Products.

The principal building materials made of fired clay are bricks, tiles and terra-cotta, but other important products are drainpipes, floor and wall tiles, and sanitary ware such as baths. The products may be glazed or unglazed. Vitreous enamelled goods, although, in a sense, ceramic materials, are not considered in the present article.

Bricks may be classified according to their intended purpose, and they then fall into the broad groups of engineering bricks, facing bricks, and common bricks. This broad classification has been adopted later when considering the properties of the finished products. In the study of manufacturing processes it is more convenient to group the products according to methods of manufacture, since some processes are common to many products.

Raw Materials and Preparation.

Common bricks can be made from almost any clay or shale provided the process is suitably adjusted to the raw material, but the other products require clays of definite characteristics such as colour, texture, plasticity, and regularity of shrinkage. The required properties are often obtained by blending several clays.

Where the clay deposit is homogeneous, mechanical excavation is possible, but in the majority of pits the diversity of the deposits renders hand excavation necessary.

After winning, the clay is ground, blended, and tempered with water, these processes having largely superseded weathering, which is too costly for all but the more expensive facing bricks, tiles and terra-cotta. Grinding is carried out (1) in pan-mills, the bottom plate of which is

either solid or perforated to act as a sieve, or (2) in "rolls" A modern method is the use of "differential" rolls, that is, mills with one roll rotating faster than the other. After being ground the clays are blended and tempered by the addition of water varying from 10 per cent in the case of dry pressed clays to 30 per cent where the clay is intended for hand moulding.

Moulding.

Clay working processes fall into three groups, viz (1) fully plastic, (2) semi plastic, and (3) dry pressed methods

The fully plastic methods are used for hand made bricks and tiles, and also terra cotta, and the heavier sanitary goods made by hand. For bricks and tiles the soft clay is thrown into a sanded wooden mould which is then removed *Various sands are used to give different textures* and colours. Terra cotta and sanitary goods are made by pressing the clay into a plaster mould which is removed after the clay has dried and shrunk somewhat

Mechanical processes of working plastic clay include the "soft mud" process which imitates hand brick making, and the wire-cut process In this latter process the clay paste containing from 15 to 20% of water is extruded through a die and the ribbon is cut into suitable lengths. This process is used for the manufacture of bricks, tiles, and all forms of hollow bricks, drainpipes, and conduits. In the dry-press process the clay containing 10% water is ground to $\frac{3}{16}$ in. or smaller and then pressed in steel moulds. The method is used largely for the manufacture of fletton bricks and wall or floor tiles Engineering and other dense bricks are often made by re pressing partly dry, but still plastic, wire-cut bricks.

Drying.

Goods made by plastic and semi plastic methods require to be dried before being fired Dry pressed goods are usually set straight in the kiln. Open air drying is in use to a great extent in seasonal yards operating from spring to autumn, but is rapidly giving way to mechanical processes where the products are dried at schedule rates under controlled conditions of temperature and humidity. The mechanical dryers may be either of the intermittent or of the chamber types, in which the goods remain stationary during the whole process, or the continuous or tunnel dryer where the goods travel on cars through a tunnel whose different sections are maintained at steady states of temperature and humidity. Terra cotta and heavy sanitary goods are dried on heated floors. During drying the goods undergo from 5 to 10% linear shrinkage. A discussion of dryers is given by Brown, "Science and Practice of Drying," Clayworker Press, London, 1933.

Firing.

The simplest method of firing is the "clamp" as used, for example, for firing London Stock bricks. A stack is built of bricks and fuel laid in alternate layers, an operation requiring great skill and experience, and the stack is then allowed to burn through. A proportion of fuel is mixed with the clay used for making the bricks. Permanent intermittent kilns are used for certain facing bricks, and most tiles and

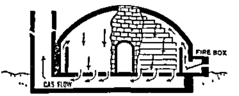


FIG. A.

terra-cotta This type of kiln is more suitable for firing goods which need varied treatment such as alternate oxidation or reduction during firing (Fig A)

The most popular kiln for brick burning is the Hofman type continuous kiln (Fig B). This

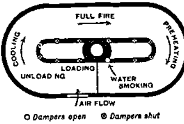


FIG. B

consists of a circular or oval tunnel round which the fire travels continuously. Fuel is usually fed through holes in the roof, and air for combustion is pre heated by being drawn over the hot fired bricks. The hot furnace gases are

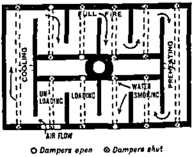


FIG. C.

drawn over the unfired bricks before being taken out to the chimney.

Developments of this kiln are the chamber kiln fired from the side, the use of producer gas instead of coal, automatic stokers for coal-fired kilns, and the Zig-Zag kiln (Fig C).

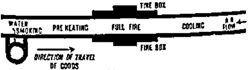


FIG. D.

The tunnel continuous kiln (Fig. D) is only used to a small extent for bricks but more commonly for firing sanitary goods. In this

kiln the fire is maintained steady at a point almost half-way along a tunnel through which the goods travel on steel cars protected by a refractory platform. During their passage the ware is slowly heated and slowly cooled.

Both types of continuous kiln are economical, consuming from 4 to 6 cwt. of coal per 1,000 bricks as compared with 10 to 12 cwt. consumed by intermittent kilns. The time of firing varies from 2 to 4 days in a tunnel kiln, from 7 to 14 days in an intermittent kiln, and from 14 days to 6 weeks for a complete circuit of a Hofman type kiln.

Descriptions of kilns are given by Singer, "Die Tunnelöfen," Berlin, 1933, and Searle, "Some Methods of Firing Continuous Kilns," Clayworker Press, London, 1929.

Firing is usually considered as divided into stages. These overlap and no distinct line can be drawn where one stage ends and the next begins. The first or "water-smoking" stage extends up to about 600°C. In the early stages up to about 200°C. the residue of hygroscopic and added water is eliminated, while at 400°C. to 600°C. the water of combination of the clay molecule is eliminated. During this stage of firing there is little or no change of size in the product, but porosity increases.

The kiln atmosphere is usually heavily charged with moisture, and the rate of heating must be slow, to permit the escape of steam from the interior of the goods.

During the second or oxidation stage, from about 500°C. to 900°C., carbonaceous matter is burnt off and carbonates and sulphides are decomposed. It is during the early part of this stage that large quantities of inflammable gases are evolved from such clays as the Oxford and Kimmeridge. In the second stage the goods attain their maximum porosity and there is a slight expansion (up to 1 per cent. of the dry length).

The rate of firing must be adjusted to permit the access of air for combustion of carbonaceous matter, and also the escape of products of decomposition. Too rapid firing at this stage may result in the formation of a vitreous skin which seals the interior, precludes oxidation, and causes black cores. These may during later stages cause swelling or bloating.

In the final stage from 950°C. upwards to the finishing temperature, the fine-grained constituents of the clay sinter together to form a glassy bond for the remainder of the product.

During this period the firing shrinkage occurs, and porosity decreases very rapidly. Shrinkage varies with different clays, but bricks fired to about 1,000° shrink from 4% of the dry length, for a coarse-textured clay, to 8% for a fine-grained clay.

Heating from, say, 950°C. is usually rapid up to the final temperature, at which the goods are maintained for some time.

Most ceramic goods are fired in an oxidising atmosphere, but, for the production of blue bricks, certain purple facing bricks, and also for salt glazing, there is a further firing period during which the previous oxidising conditions are changed to reducing conditions. This causes the conversion of the red and brown ferric compounds to blue or grey ferrous compounds, which, being fusible, produce a dense glassy structure in clays rich in iron.

Salt glazing is carried out by casting salt into the kiln when the temperature is 1,200°C. or over, and the atmosphere is reducing. The volatilised salt reacts with the clay to form a glassy surface skin of sodium-alumino-silicates (Thompson, Trans. Cer. Soc. 1918, **17**, 340).

The process is used mainly for sewer pipes and some chemical stoneware. Other products are glazed by usual pottery methods using felspathic leadless glazes. Coloured roofing tiles are glazed with opaque stanniferous galena glazes tinted with suitable oxides.

The approximate firing temperatures of different materials are given in the table below:

Approximate Firing Temperatures for Different Classes of Ceramic Products.

Product.	Firing temperature.
Hollow partition blocks	850°C.–1,000°C.
Common and facing bricks, roofing tiles	950°C.–1,100°C.
Floor and glazed wall tiles	1,000°C.–1,100°C.
Engineering bricks, terra-cotta	1,050°C.–1,200°C.
Glazed fireclay sanitary goods and glazed pipes.	1,100°C.–1,200°C.
Salt glazed goods	1,200°C.–1,300°C.

Recent years have seen marked advances in the control of drying and firing, and increasing numbers of works are equipped with humidity and temperature recorders for controlling dryers; recording pyrometers, CO_2- and draught-meters are used on kilns. In many cases also draught is maintained by fans rather than by chimney draught. These enable waste heat from the kilns to be used for drying the wet goods. Despite the greater control now exercised ceramic goods are still liable to certain faults.

Faults.

Defects in clay products arise either from defective processes or from the use of poor or unsuitable clays. Wire-cut products may be laminated owing to the presence of air films in the raw moulded brick. A recent innovation is the removal of the air by evacuation. Although the "de-airing" process is said to be of particular benefit in the production of drainpipes, the process is not suited for all clays. A cause of cracking and lamination in dry-pressed goods is excessive pressure, while too slight pressure or too dry a mix gives a product which is friable and soft centred.

Too rapid firing or drying causes the development of cracks as well as the black core already mentioned.

Nodules of limestone and gypsum in clays burn to lime and anhydrous calcium sulphate respectively, and may cause disruption when the products are exposed, due to the expansion

ensuing on hydration Such clays require to be finely ground.

The kiln gases invariably contain sulphur dioxide, which is capable of reacting with the clay constituents and causing the formation of soluble salts which will, later, give rise to unsightly or dangerous efflorescences in the brick. The rate of formation of these compounds is most rapid at about 700°C and high firing *temperatures tend to their elimination* Alkali sulphates are eliminated fairly readily, but calcium and magnesium sulphates are only eliminated by prolonged firing at over 1,050°C. (Simon and Vetter, Z angew. Chem. 1930, 43, 380; Brady and Coleman, Trans Ceram. Soc. 1931, 30, 169, 1932, 31, 58).

Efflorescence of soluble salts formed in this way should be *distinguished from scum which is* formed during the manufacture of the brick. Soluble salts present in the clay may be drawn to the surface during drying and cause "dryer scum" When due to calcium compounds such as gypsum, it can sometimes be prevented by additions of barium carbonate to the clay, giving insoluble calcium carbonate and barium sulphate. Kiln scum is caused by the action of sulphurous gases on the unfired ware during the early stages of firing when moisture is present in the kiln gases Calcareous clays are most affected Soluble compounds are formed on the surface of the goods and burn to give a white scum. Unlike efflorescence, scum has no effect on the durability of the brick.

Products carrying an applied glazed surface are liable to crazing or peeling if the coefficients of thermal expansion of the glaze and body are different Crazing of glazed wall tiles is some times due to moisture expansion of the body or shrinkage of the cement backing (Mellor, Trans. Ceram. Soc. 1935, 34, 1).

The following references are to sources of information on the manufacture of structural clay goods.

Searle, "Modern Brickmaking" (E. Benn, Ltd), London, 1931.

Zaiman and McIntyre, "Economic and Manufacturing Aspects of Building Brick Industries," Building Research Special Report No. 20 (H.M. Stationery Office), London, 1933.

Zaiman and McIntyre, "Manufacture of Clay Roofing Tiles in France, Holland, and Belgium," Building Research Bulletin No. 4 (H.M. Stationery Office), London, 1928.

Dummler and Loeser, "Handbuch der Ziegelfabrikation" (W. Knapp), Halle, 1926

Granger, "La Céramique Industrielle," 2 vols (Gauthier-Villiers), Paris, 1929.

The Properties and Testing of Building Bricks.

(*a*) *Engineering Bricks*.—The properties of most importance in bricks used for engineering purposes are high strength and low porosity. The range of compressive strengths of bricks used for engineering work is approximately from 5,000–16,000 lb. per sq in ; the porosity varies from below 1% to about 18% (by volume), *or 8% if the porosity is expressed in terms of the weight* of water absorbed.

Engineering bricks are also highly acid-resistant—a property which is occasionally of importance in building.

Many bricks which would be suitable for engineering purposes are also used as facing bricks, especially in the north of England. In such cases the critical tests are not strength and porosity, but those which attempt to assess properties having a more direct bearing on their use as facing bricks (*see* below)

(*b*) *Facing Bricks*.—In bricks used for ordinary building purposes it is unnecessary to consider mechanical strength because even the weakest bricks in common use possess sufficient strength to meet all the demands likely to be made upon them. (Strengths as low as 1,000 lb. per sq in are not uncommon, particularly amongst hand-*made facing bricks such as London stocks*, which, nevertheless, are very weather resistant) There are certain other properties in respect of which the characteristics of bricks as a class are so well known that formal testing is rarely necessary ; such are heat and sound insulation There is an approximate relation between bulk density (weight divided by overall volume including pore space) and thermal conductivity which is given in the following table taken from Tonind.-Ztg 1932, 56, 1044:

TABLE 1.

Bulk Density.	*Thermal Conductivity*
1 8 kg./cdm.	0 55–0 60 cal./m hr.°C
1·6 ,,	0 40–0 45 ,,
1 2 ,,	0 23–0 27 ,,

In considering the suitability of bricks for use for facing it is more important to study the chemical and physical properties which determine their serviceability. The most important in the case of facing bricks are resistance to rain penetration and resistance to weathering. The question of freedom from soluble salts likely to form efflorescences is of importance in the case of both facing and backing bricks and will be considered in a separate section.

There are two ways in which a wall may exclude water. One is by presenting an impervious skin to the rain. This method finds more favour in Germany than in England and has been discussed by W Thein (Diss. Brunswick, 1931) The method makes exceptional demands upon the workmanship of the bricklayer, since imperfect bonding of bricks and mortar, which may easily occur with highly vitrified bricks, leaves cracks through which water may penetrate to the more porous backing bricks. The impervious nature of the facing bricks then becomes a disadvantage, preventing the water from again drying out through the face of the wall. *The other method, which is more* in accordance with British and especially southern English practice, depends on the use of a moderately porous brick which bonds well with mortar and has the merit of allowing the water which it absorbs to be evaporated rapidly (*cf.* L. F. Cooling, Trans. Ceram. Soc. 1929, 29, 39). A wall built of such bricks absorbs water by capillary forces, its pore space *acting as a* reservoir in which the water is held until it

can again be evaporated. The extent to which this capacity to hold water can be relied upon to keep the inside of a wall dry in any given situation is fairly well understood empirically. In some situations this capacity is insufficient and where exposure is severe, as on a south-west elevation, in Great Britain, facing the sea, walls are either built with a cavity or are rendered. It must be emphasised that bricks of the same porosity may differ widely in permeability, and that the latter property must be measured in order to decide whether a given brick needs to be used with special precautions. Table 2 gives the porosity and permeability of a hand-made facing brick (exceptional) which gave rise to serious rain penetration, and comparative figures for bricks of more normal properties.

TABLE 2.

POROSITIES AND PERMEABILITIES OF FACING BRICKS.

Brick.	Porosity (% by vol.).	Permeability under 20 cm. head of water c.c./sq.cm./sec. $\times 10^6$ after					
		5 min.	10 min.	30 min.	1 hr.	2 hrs.	24 hrs.
Hand-made brick (exceptional) . .	27·3	3,582	3,346	3,037	2,779	2,480	—
Hand-made red brick	33·7	840	640	399	294	222	12
Dry pressed red brick	27·2	1,703	1,191	215	207	207	—
Plastic pressed red brick	19·7	233	184	100	62	33	2·5

It should be added that these very permeable bricks are rare and that rain penetration is more often due to faulty workmanship, especially failure to fill vertical joints, or to faulty design, than to penetration of water through the body of either brick or mortar. This aspect of the subject has been discussed by F. O. Anderegg (Brick and Clay Record, 1931, **79**, 291).

Knowledge of the mechanism of weathering in bricks is incomplete. It is not yet possible to lay down standard methods of test which will assess the probable durability of a brick without making demands upon the investigator's experience of the materials. The most important obstacles to the development of improved tests are the following: in many cases the results of laboratory tests have not been adequately compared with exposure tests under natural conditions owing to the slowness with which the natural weathering of good bricks takes place; it is not even possible to compare results with reputations based on the study of old buildings, because bricks made by modern methods differ from older bricks even when the clays are the same. A further difficulty is uncertainty as to the effective weathering agent, which may vary with the climate. Workers in Germany, Sweden, and the U.S.A. have regarded frost as the principal weathering agent (*cf.* the use of adsorption ratio as a criterion of weather resistance), but it may be doubted whether it is the dominant factor in England except in certain situations such as retaining walls or parapets. The evidence for attack by atmospheric acids upon building bricks is slight. Indeed, it may be said that the majority of English bricks do not weather in the face of a wall, although there are a few types, notably certain soft red bricks, which crumble away from the face and require to be replaced in the course of a few decades. In these cases the primary cause of weathering may well be hydrolysis as suggested by C. E. Moore (Claycraft, 1933, **6**, 381) by analogy with the weathering of rocks in nature. Moore pointed out that bricks fired at temperatures below about 950° C. would be expected on theoretical grounds to be more susceptible to the action of water than those fired at higher temperatures.

On account of these difficulties the present starting point for all attempts to assess weathering quality is the generalisation, based on universal experience, that a well-fired brick is weather-resistant. This has led to the use as quality tests of measurements of properties which vary or are assumed to vary as functions of firing temperature. Of these properties strength and water adsorption have been most studied, but no clear estimate of quality can be based upon them. Whilst there is in general an increase in strength and a decrease in porosity as the firing temperature of a clay is advanced, the differences between bricks made from different clays and by different manufacturing processes are such that it is impossible to lay down any limits which would separate good bricks from bad. The subject of water adsorption and of the various attempts that have been made to improve upon the simple test of adsorption capacity was reviewed in some detail by C. M. Watkins and B. Butterworth (Trans. Ceram. Soc. 1934, **33**, 444). A tentative specification of the American Society for Testing Materials published in 1935 has proposed the use of a combination of properties, compressive strength, absorption, and absorption ratio, as a means of separating well-fired from underfired bricks. The basis of the specification is the extensive survey of the properties of bricks made in the U.S.A. carried out by McBurney and co-workers (Proc. Amer. Soc. Testing Materials, 1933, **33** (Pt. 2), 636, and previous papers). The limits proposed in that specification would not be applicable in Great Britain, where a large number

of hand-made bricks are still made, whereas in the U.S.A. the number is negligible. Hand-made bricks generally have lower strengths than machine-made bricks, and most hand made bricks would be rejected by the *A.S T M.* specification in spite of their excellent weathering properties.

The tests most relied upon in this country are (1) resistance to the crystallisation of sodium sulphate and (2) expansion on wetting; freezing tests are also carried out, but their results are less informative because an entirely satisfactory method of carrying out the test is still to be found The sodium sulphate crystallisation test gives a comparison between different bricks in respect of resistance to expansive stresses set up within their pores. If a standardised method of carrying out the test is adopted it is then possible to judge the quality of a brick under test by comparing its performance with that of other bricks of known quality.

The linear expansion on wetting of well fired bricks ranges from 0 005 to 0 025%; much higher values, of the order of 0 06%, are associated with under firing, though bricks showing an expansion of this order are seldom put on the market.

(*c*) *Backing Bricks*.—Bricks which are only used internally in a building or which if used externally are covered with a cement rendering need not be so weather resistant as facing bricks. The principal requirement is that they should afford a good key for plaster This involves the possession of a certain degree of porosity, but the rate of adsorption should not be too great or the plaster will be dried out too soon after application; a very smooth surface is also a disadvantage. To improve the *mechanical key for plaster, certain bricks are* specially grooved.

Freedom from soluble salts is also important, *see* below.

(*d*) *Efflorescence*.—Soluble salts present in masonry may migrate in solution and crystallise on or beneath the surface when the water is evaporated. Slight superficial efflorescences are common on facing bricks in new buildings; the salts may be derived either from the bricks or from the mortar. Such efflorescences are usually dispersed by the action of wind and rain in a very few years, and are chiefly in evidence in the spring More important are the phenomena which may result from the presence of the considerable quantities of $MgSO_4$ which occur in some underfired bricks. Plaster applied to *such bricks may separate with a thin lamina of* brick adhering to it owing to the formation of a semi-permeable membrane of $Mg(OH)_2$ at the point where the sulphate first comes in contact with lime derived from the plaster. When the water evaporates needle-shaped crystals of $MgSO_4,7H_2O$ form behind the membrane with their long axes at right angles to the wall (F. L. Brady, Nature, 1930, **126**, 684). $MgSO_4$ is also capable of causing failure of the bricks themselves when present in large amounts

Sulphates generally are dangerous in common bricks because of the liability to injure cement renderings applied to them. Much depends on the exposure of the brickwork and upon weather conditions during building. In work which contains much water, the sulphates may pass to the junction of the brickwork and cement *rendering and cause detachment. Under dry* conditions there may be no trouble even with brickwork having a high sulphate content.

Estimation of the total percentage of water soluble matter in a brick is no guide to its tendency to form efflorescences, because the greater part of the soluble matter generally consists of $CaSO_4$, which is inert from an efflorescence point of view. Even bricks containing much $MgSO_4$ usually contain more $CaSO_4$. It is not yet possible to lay down a rigid limit for soluble salt content, but it is thought that trouble may occur with bricks containing more than 0 05% Mg. When carrying out a soluble salt analysis it is essential to extract a fine powder (passing a 100 mesh sieve) by agitating thoroughly with an excess of *water and washing well in order to extract the* salts completely. Erroneously low results have been published owing to failure to ensure complete extraction Table 3 shows some typical soluble salt analyses of reputable English building bricks, (1)–(8); one analysis (9) of a brick known to give serious $MgSO_4$ efflorescence is added for comparison.

It is uncertain whether the alkalis are present as sulphates or whether they are not derived in part at least from a slight hydrolysis of silicates during the extraction.

The soluble salt analysis may with advantage be supplemented by a direct efflorescence test which consists in feeding the brick with distilled water at room temperature and then allowing it to dry out Salts dissolved by the water in *passing through the brick are deposited on the* surface as an efflorescence (B. Butterworth, Trans Ceram Soc. 1933, **32**, 270).

Tiles.

There is a British Standard Specification for clay plain roofing tiles which lays down tests of permeability, transverse strength, and resistance to freezing (B.S S, No. 402—1930).

The principal defect shown by many tiles is a tendency to exfoliate after some years' exposure *owing to the effect of frost.* This effect is more common with machine-made than with hand-made tiles. Exfoliation may be reduced by avoiding certain faulty methods of fixing tiles which tend to keep them unduly wet. The merits of various current methods of using tiles have been discussed by *L. G. Tomlinson* (Trans. Ceram Soc. 1929, **29**, 1).

Terra Cotta.

Terra cotta is comparable in physical structure with engineering bricks. A study of the weathering of terra cotta was made by W. A. MacIntyre (Building Research Special Rept. No. 12, 1929). MacIntyre found that the decay of much of the terra cotta used in London about the middle of the nineteenth century was due to *underfiring. Underfired* material was extensively used owing to the popularity with architects of a certain shade of colour which could only be obtained by underfiring.

TABLE 3.

SOLUBLE SALT ANALYSES OF SOME ENGLISH BRICKS.

Brick.	Rustic wirecut.	Gault facing.	Fletton.	Red wirecut.	London stock hand made.	Plastic pressed red.	Purple multi hand made.	Buff facing.	Soft common wirecut.
Source.	Yorks.	Kent.	Nr. Peterborough.	Leicestershire.	Bucks.	Lancs.	Herts.	East Midlands.	S.E. England.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Total soluble salts (dried at 110°C.)	0·94	0·84	3·16	0·94	0·74	0·11	0·10	0·29	3·89
Ca . . .	0·19	0·17	0·80	0·21	0·15	0·01	0·00	0·04	0·60
Mg . . .	0·03	0·01	0·01	0·01	0·02	0·01	0·01	0·00	0·25
Na . . .	0·04	0·02	0·04	0·03	0·04	0·03	0·04	0·01	0·06
K. . . .	0·02	0·04	0·03	0·03	0·01	trace	0·00	0·02	0·04
SO_4 . . .	0·48	0·39	2·07	0·50	0·34	0·04	0·04	0·07	2·62
SiO_3. . .	0·03	0·04	0·02	0·04	0·05	0·02	—	0·02	0·03
Liability to efflorescence	*slight*	*slight*	*nil, but $CaSO_4$ may be lost by diffusion*	*slight*	*nil or slight*	*nil*	*nil*	*nil*	*serious*

Salt-glazed Pipes.

British Standard dimensions of drain fittings are specified in British Standard Specification No. 539, 1934. Specifications referring to quality are British Standard Specification No. 65, 1934, and British Standard Specification No. 540, 1934. Impermeability, hydraulic, and absorption tests are laid down.

B. B. and E. H. C.

II. CALCIUM SULPHATE PLASTERS AND CEMENTS.

Nomenclature.

The calcium sulphate plasters are those cementitious materials employed in building and in the arts, which have a definite set solely due to hydration of calcium sulphate, in some form; they may be anhydrous or contain a certain small proportion of combined water.

They are sometimes known as "gypsum plasters," since most of them are prepared by calcining gypsum, and all revert wholly or partially to gypsum when set; the harder are termed "cements." A large proportion are marketed under proprietary names and certain traditional names or modifications of the same. Unfortunately these names often afford no clue as to the type and composition, and there is no assurance that a material sold under a certain name will continue uniform.

Raw Materials.

Apart from minor recent sources in by-products of other industries, such as precipitated gypsum from the phosphate industry, the main source of the raw material of the calcium sulphate plasters is either mineral gypsum, $CaSO_4,2H_2O$, or (latterly) natural anhydrite, $CaSO_4$.

The British gypsum deposits are mainly associated with the keuper marls, and are usually thin-bedded; the principal sources are in the valleys of the Trent, and of the Eden in the Carlisle district, though fairly thick beds of a grey gypsum associated with limestone and shale are mined in one locality in Sussex. Anhydrite is a common impurity. Massive beds of natural anhydrite are found near Hartlepool and Middlesbrough, and are mined on a large scale at Billingham, both for plaster manufacture and for use in the heavy chemical industry.

Only a comparatively small proportion of the gypsum used is imported, and that mainly for use as Portland cement retarder.

Calcination of Plaster.

From gypsum the various plasters and cements are prepared essentially by partial or complete dehydration by means of heat. The different grades are obtained mainly by varying the degree (temperature and duration) of calcination, by calcining either before or after grinding, and by various additions made to the ground and calcined material (catalysts of set, accelerators or retarders). Natural anhydrite is already anhydrous, so requires no calcining: it is merely ground, and accelerator added.

The table on p. 130 gives a key to the successive products of calcination of gypsum, the associated materials, and the properties which may be used in recognising them in plasters.

The crystallised product (7) is readily obtained by heating gypsum in water under pressure above the equilibrium point at 107°C. (or at a proportionately lower temperature in a suitable salt solution), rapid filtering whilst hot, and washing with absolute alcohol. It is readily soluble in water, hydrating to gypsum like (2).

The results of a number of investigators with X-ray analysis suggest three different crystal

No	Product and composition	Preparation, temperature of calcining	Crystal form	Density	Refractive Index.	Bi refringence.	Extinction
1.	Gypsum, $CaSO_4,2H_2O$	Mineral; product of set.	Monoclinic (rhomboids, arrow head twins)	2 2 −2 3	α 1·5207 β 1 5228 γ 1·5305	Small	Oblique
2.	Hemihydrate, $(CaSO_4)_2,H_2O$	Calcining gypsum below about 190°C in open kettle or pan.	Pseudo morph of original gypsum.	2 66	1·54 −1·56		Rectangular.
3.	Soluble anhydrite, $CaSO_4$.	Calcining gypsum up to 200° − 300°C. or at lower temp. in a stream of dry air [1]	,,	2 4 −2 6	1·50 −1·54		,,
4.	"Insoluble" anhydrite, $CaSO_4$	From (3) above about 300°C gradual irreversible con version.[2]	,,	2 8 −3 0	1·55 −1 57		,,
5.	Natural anhydrite, $CaSO_4$.	Mineral	Orthorhombic.	2·8 −3 0	α 1·571 β 1 576 γ 1 614	High: marked play of colours.	,,
6	Estrichgips, $CaSO_4$ and CaO.	Calcining gypsum at approaching white heat.	(Partly sintered.)				,,
7.	Crystallised hemihydrate, $(CaSO_4)_2,H_2O$	Wet method.	Long, slender needles, described as trigonal.	2 64	1 569 1·586		,,

[1] A gradual and reversible loss of water, a "zeolitic" change.
[2] Product depends on temperature and time of calcining.

(3) is extremely hygroscopic, reverting immediately to (2).
(4) is inert, and almost insoluble.

lattices. that of (1); that of (2), (3), and (7); and that of (4) and (5) respectively.

The impurities in the natural rock will also be modified by calcination; when "hard burnt" at a temperature in the neighbourhood of a red heat, calcium carbonate will be partly converted into free lime which may also be produced by partial dissociation at higher temperatures. Commercial plasters are necessarily somewhat mixed products.

Manufacture.

Where gypsum is used the principal manufacturing operation is that of calcination. The commercial calciners are of numerous types. For hemihydrate (plaster of Paris) the deep American kettle, holding 5–10 tons of ground gypsum at a charge, fitted with stirrers and cross-flues for direct firing by coal, gas or oil, is commonly used, with a calcination cycle of 1½ to 3 hours In Great Britain the shallow, open pan is still used to some extent, fitted with a stirring rake and taking a much smaller charge in a similar cycle. Numerous patents have been granted for various methods of direct and indirect heating, by superheated water, hot oil, etc; rotary kilns of various types are employed, particularly in America and in Germany, usually fitted with lifting devices and with (at least partly) co-current heating so as to avoid overheating of the product which might occur if arranged in the conventional manner of a cement kiln with counter-current of hot gases and calcined product. A modern development is the simultaneous grinding and dehydration (by hot air) in the same mill.

The "hard burnt" or anhydrous plasters are usually calcined, in lump form, and ground afterwards, the necessary accelerator being added at one stage or another. In order to preserve a light colour, and to avoid the introduction of fuel ash, modern British anhydrous plasters are usually burnt in separate-fired continuous vertical kilns, although mixed-feed vertical kilns both of the continuous and of the batch type have been employed widely in the past, and some are still in use in other countries. On account of the low thermal conductivity of gypsum, and of the endothermic nature of the dehydration process, the larger lumps are seldom calcined to the same degree throughout, so that there may be unchanged gypsum, hemihydrate, and soluble anhydrite in the middle of a lump when withdrawn, and at the corners and edges the rock may be overburnt, and even partly dissociated into free lime.

"Boiled Keene's" is still made by heating ground gypsum, with some stirring, on an open hearth under which flues pass, with a temperature approaching a red heat in parts, an accelerator being added and the heating then finished. The German "Estrichgips" or flooring plaster is calcined in vertical kilns in lump form at a high temperature (attaining 1,100°–1,200°C.), so that some dissociation results and a small amount of free lime is left intimately mixed with the product. Ovens resembling baker's ovens are employed on the Continent for calcining certain types of plaster.

Setting of Plaster.

The setting of a calcium sulphate plaster or cement is essentially a process of recrystallisation, *i.e.* the formation of hydrated crystals of gypsum from a supersaturated solution. These crystals are tangled and interlocked, and grow together, thus forming a rigid crystalline structure of set plaster, embedding the sand grains or other aggregate present, but often (especially with hemihydrate plasters) leaving a proportion of voids. The strength and hardness, and texture of surface, will depend on the rate of growth, *i.e.* on the shape and size of these crystals, and on their closeness of packing.

The hemihydrate possesses a solubility about five times that of gypsum, so that when mixed with water it rapidly dissolves to form a solution heavily supersaturated with respect to gypsum. If crystal nuclei of gypsum are already present (as is usually the case with plaster of Paris calcined in an open pan at a comparatively low temperature), within a very few minutes crystallisation of gypsum commences at these nuclei, and spreads rapidly throughout the mass. As the concentration of the solution tends to decrease, more hemihydrate goes into solution, and is precipitated in turn as gypsum; this process continues until all the hemihydrate is consumed, or until no water is left. In a workable plastering mix the water will be present in great excess over the stoichiometric equivalent.

In the case of anhydrous plasters, *i.e.* "hard burnt" or natural anhydrite, the process of setting is analogous to that of the hemihydrate, but the degree of supersaturation achieved is very much less. Setting takes place much more slowly and only at an appreciable rate in the presence of a suitable catalyst. The system "insoluble anhydrite"/water/gypsum must therefore be unstable at ordinary temperatures, but we cannot really speak of a definite "solubility" of the anhydrite in these circumstances, although it appears to be greater than that of gypsum. The rate of solution probably to a large extent controls the velocity of the reaction; fine grinding of the anhydrite is essential. A smaller proportion of mixing water is usually required by anhydrous plasters to produce a workable mix; this influences the texture of the product.

Catalysts of Set. (Accelerators and Retarders.)

Since ordinary plaster of Paris starts to set too quickly for convenient application for plastering (in sanded undercoats) and for some other uses, a retarder of set is frequently added, ordinary glue or size being employed on a small scale and "keratin" (sodium and calcium salts of the amino acids resulting from the partial hydrolytic degradation of the proteins of horns, hoofs, and hair) in many "hard wall" plasters. These act apparently by being adsorbed on the nuclei (of unchanged gypsum, dust, etc.) which would normally provide a start for the recrystallisation of gypsum, and in this way, and by retarding the diffusion of fresh material inwards to build up the crystals, delay the onset of effective "setting." Once this starts, and the crystal has outgrown its shell of adsorbed glue, etc., the setting takes its normal course. Thus the retarded hemihydrate plasters can be described as comparatively slow-starting but rapid-setting. The proportion of retarder needed is minute: about ½ lb. to 10 lb. per ton of plaster being the range of usual proportions which retard the "set" to a convenient period for normal use. Borax is also occasionally employed as a retarder (about 1 or 2 per cent. in solution or as a solid); the action of this salt is somewhat obscure.

The accelerators of set employed with the anhydrous plasters are usually soluble sulphates. Potassium sulphate is the commonest, either alone or as potash alum. Soluble sulphates of other metals are also employed, *e.g.* aluminium or zinc sulphate, or mixtures of these. As a rule sodium salts (though otherwise effective) are to be avoided, as these tend to produce unsightly efflorescences. The precise action of accelerators is still a matter of surmise, although much has been written on this subject; the simple theory of the effect on the solubility of gypsum leads to contradictions. The set is usually adjusted so as to give an "initial set" in a couple of hours, *i.e.* the plaster is slow-starting; the hardening then proceeds slowly, and in some cases may take several weeks to complete in damp storage, particularly with natural anhydrite plasters and those accelerated with lime in place of soluble alkali salts.

Lime acts *per se* as an accelerator of set. It is less active than soluble sulphates, and may, of course, lose its effectiveness in long storage, owing to neutralisation by atmospheric carbon dioxide.

It follows from the above that the removal or neutralisation of the glue or salt used for adjusting the set will have the opposite effect in retarded or accelerated plasters, accelerating the former and retarding the latter. In general the loss of acceleration from the anhydrous plasters is more often encountered and more serious in its effects than the removal of glue from retarded plasters

Expansion.

Although there is a decrease in total volume of about 7% in the hydration of plaster to crystal line gypsum, *on account of the thrust of the growing crystals, and of the porous structure of* the set plaster resulting, there is a linear expansion of approximately 0 2 to 0 4% during the setting of a paste of plaster and water, if unrestrained This expansion enables very sharp casts in plaster to be made A comparatively small restraining force can inhibit the movement in any one or two directions Under certain conditions this expansion can produce unwelcome effects (" delayed expansion ") The extent of the expansion depends on the circumstances *of setting, and particularly on the* presence of accelerators or retarders. In order to obtain a very small expansion combined with a convenient setting time for dental casts, both accelerators (potassium salts) and retarders (*e g.* borax) have been used simultaneously with plaster of Paris.

Corrosion.

Ironwork in contact with moist calcium sulphate is corroded, and especially with some calcium sulphate plasters of the "acid" type, *i e* those accelerated with alum. On the other *hand, those plasters containing free lime act (for a time) as definite protective agents* to embedded iron. In general, metal work (except perhaps lead) should be protected from contact with plaster, if there is any risk of damp.

Classification.

The appended table indicates the classification of modern calcium sulphate plasters and cements. This cannot be applied in every case, since the practice of different makers varies.

CALCIUM SULPHATE PLASTERS.

Composition.

Group 1 Accelerated Anhydrous $CaSO_4$	Group 2. Hemihydrate $(CaSO_4)_2,H_2O$
i From gypsum calcined at or above a red heat ii From natural anhydrite, $CaSO_4$	From gypsum calcined below about 190°C.
A. Accelerated with lime Proprietary plasters hard-burnt from gypsum containing much $CaCO_3$ Estrichgips.	A Retarded hemihydrate. Many proprietary "hard wall" plasters for trowel application (usually keratin retarded). Plaster of Paris retarded with glue, size, or borax for decorative plaster work.
B. Accelerated with soluble salts. Most proprietary "hard burnt" plasters for trowel application (usually accelerated with alum or K_2SO_4). Natural anhydrite plaster (accelerated with sulphates). Most "Keene's"[1] and "Parian" cements. "Substitutes for Keene's"	B. Unretarded. Plaster of Paris. Common "gauging plaster." Casting plaster. Surgical and some dental plaster. Ceramic moulds. Plaster for ornamental work, fibrous plaster ("stick and rag"), plaster wall boards, building blocks, and tiles.
Some extra hard dental moulding plasters may be of Group 1.	Certain special non-expansive dental plasters for impressions are plaster of Paris simultaneously accelerated and retarded.

Setting.

1 A	1 B.	2 B	2 A.
Start: Slow, if of uniform composition.[2]	Slow.[2]	Quick.	"Undercoat," Slow; "Finishing," Medium-slow.[3]
Completion: Slow. If lime % is low very slow.	Slow.	Quick.	Quick.

[1] The original "Keene's" was double-burnt, and alum-accelerated
[2] Certain brands contain a portion of quick starting material (soluble anhydrite, $CaSO_4$, and hemihydrate)
[3] With lime, somewhat quick.

III. Lime.

Classification.

Lime is employed in vast quantities in building; as a cheap alkali in the heavy chemical industries; as a flux; for water softening; in tanning, etc.; and in agriculture. For standard specification purposes " lime " may be defined as consisting essentially either of calcium oxide, CaO, or of calcium oxide together with a smaller proportion of magnesium oxide, MgO, formed by burning a natural rock or other suitable material at such a temperature that it will slake when brought into contact with water. The raw material for building limes may sometimes be of a composition approaching dolomite ($MgCO_3$,$CaCO_3$).

The term also includes in practice dry hydrated limes prepared in the form of a fine dry powder by treating quicklime with sufficient water to satisfy the chemical affinity of the free calcium oxide present whilst producing a dry, sound product, *i.e.* essentially $Ca(OH)_2$.

Lime for chemical purposes requires, in general, to be much purer than many commonly used building limes, and for certain trades a high magnesia content is undesirable: the value may be assessed on the basis of CaO content, or of lime freely soluble and " available " for some specific purpose, such as neutralisation or precipitation. For agricultural purposes finely divided calcium carbonate may be included in the term, but here again a CaO content is generally the important consideration.

The principal basis of differentiation for the British building limes is that of degree of *hydraulicity*, which depends mainly on the proportion of clay matter, hydrated aluminium silicate (represented approximately as Al_2O_3, $2SiO_2$,$2H_2O$, but actually of varied and complex composition) present as an " impurity " in the stone. Another basis for classification is that of *use*: into (i) limes suitable for plastering, for the finishing coat (and also incidentally for plastering undercoats, or " coarse stuff "); and (ii) limes suitable primarily for mortar, for masonry, or for " coarse stuff " only. The difference is mainly that of workability of the material under the craftmen's tools. A subdivision into hydraulic and non-hydraulic can be further introduced into the " mortar " class (ii). Hydraulicity is usually ignored when classifying plastering (finishing coat) limes (i).

Limes are sometimes popularly classified with " fat " and " lean " limes, the former term indicating that a plastic putty of high moisture content results on slaking, the latter the converse effect. It is often supposed that all fat limes are non-hydraulic and all lean limes hydraulic, but there are numerous exceptions.

Raw Materials.

Apart from certain by-product calcium carbonate, and cases where compounds of lime are recovered in some cyclic process and reburnt in the same works, most lime is derived by burning of limestone (hard stone or chalk) in suitable kilns, and for economic reasons the locally available limestone is invariably employed. Great Britain is extremely rich in limestones, both in quantity and width of distribution, and in variety of composition and types. Table 4 on p. 134 indicates roughly the more important of these; relatively small amounts of other deposits (*e.g.* Devonian and Silurian) are employed for local trade only. Freight rates, and rapid deterioration of quicklime through exposure in transit prevent much exchange from one region to another, though dry hydrated limes tend to find a wider market.

Composition.

Type 1.—The " high calcium " limes vary from over 98% CaO with some mountain limes (calculated on the ignited specimen), to a little under 95% for pure white chalks; the balance will be mainly silica, a little alumina, and magnesia.

Type 4.—Magnesian limes are defined as those containing over 5% MgO; but most of the British magnesian limes approximate to the proportions of dolomite, *i.e.* 35–40% MgO, with a little silica and iron. A few specimens of the " lean " type may contain more silica and less magnesia.

Type 2.—The moderately hydraulic limes (known in the south-east of England as " greystone " or " grey " limes, which must be distinguished from the " stone " lime of the Midlands, which is high calcium mountain lime, and from the " grey " lime of the West Country, which may be a liassic lime) have up to 12 or 15% of " soluble " silica and alumina, with usually a low magnesia content and some iron.

Type 3.—The eminently hydraulic limes, generally derived from thin-bedded deposits rich in clay and shale, are of variable composition, and may contain up to 30% of " soluble " silica, up to 7 or 8% of alumina, but usually not over about 2% of magnesia. The CaO content thus ranges from about 50 to 75%, though some Blue Lias limes (3 (*a*)) may show up to 80% CaO, thus overlapping the greystone limes. Those with the lowest CaO content are virtually " natural cements."

Manufacture.

The manufacturing processes are comparatively simple, and consist in: (*a*) " burning " the rock or other raw material in some type of kiln; (*b*) sorting and picking (and occasionally grinding) the quicklime produced; and (*c*) (in the case of a dry hydrated lime) hydration of the quicklime with a limited amount of water, storage for a short period, and sifting or air separation to remove coarse, unslaked particles and unsound material.

The " burning " is the dissociation by heat of the calcium (and magnesium) carbonate into " lime," CaO (and MgO), and carbon dioxide, requiring approximately 770 B.Th.U. per pound (less for magnesia). The temperatures used range from about 900°C. for hydraulic limes to 1,200° or even 1,400°C. in the case of high calcium mountain limes burnt in primitive mixed-feed kilns. The types of kiln are legion—intermittent and continuous, mixed feed and " separate feed " (*i.e.* separately fired, by coal

TABLE 4.

PRINCIPAL BRITISH LIMESTONES BURNT FOR LIME.

Variety.	High Calcium.			Magnesian.	Hydraulic.			
CHEMICAL COMPOSITION.	Mainly $CaCO_3$			$CaCO_3$ and $MgCO_3$	$CaCO_3$ and varying proportions of clay-matter ("$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$")			
TYPE		1		4	2. Moderately Hydraulic	3. Eminently Hydraulic		
						(a)	(b)	(c)
DESCRIPTION.	Mountain	White Chalk	Oolitic [1]	High Magnesian (Dolomitic)	Greystone	Blue Lias	Chalk Marl	Scotch (shaley) Carboniferous
GEOLOGY	Carboniferous (Massive)	Upper Cretaceous (Upper Chalk)	Oolitic	Permian	Upper Cretaceous (Lower Chalk)	Liassic	Lower Cretaceous	Carboniferous (thin-bedded)
PRINCIPAL DISTRICT OF ORIGIN.	Buxton, Mendips, Forest of Dean, S. Wales and N. Wales	Thames Basin, S.E England, Yorkshire, E. Anglia	Oolitic belt (Bath, Portland, etc.[1])	Narrow Permian belt, South Shields to Mansfield and Nottingham	Thames Basin (home counties)	Liassic belt (Rugby, Barrow, Aberthaw, Bridgend and in Somerset)	Cambridgeshire	S Scotland (Glasgow district)

[1] Mainly used for building stone.

or producer gas), rotary, and chamber kilns all being employed.

The hand-picking and forking of the burnt lime is almost the only quality control in general use, removing fuel ash (in mixed feed kilns), overburnt and underburnt stone: a picking belt is employed in the most modern works. On account of the short-sighted demand for large lump lime in building there is a heavy wastage *in smalls*, some of which waste is now being avoided by dry hydration and the sale as hydrate. Care is needed, therefore, to see that no rubbish goes to the hydrator.

Slaking Conditions.

Slaking, or hydration of CaO to $Ca(OH)_2$, necessarily precedes most employment of lime. For strictly chemical purposes, the precise physical condition of the slaked lime may be a matter of indifference. For some purposes, however, rapid setting may be required; for others, and especially for use in building, very small particle-size, slow setting, and high bulking are demanded. The rate of setting, the "volume-yield," and the plastic working qualities of the lime putty have been found to depend to a large extent on the precise slaking conditions employed, so that both for practical purposes (as outlined below) and for standard test purposes, a set of conditions adjusted precisely to the type of lime is adopted. The optimum conditions may vary according to the conditions under which the lime has been burnt. The amount of residue left after slaking will also depend on the method of slaking; the aim when the lime is to be employed in building is to obtain as small a residue as possible consistent with the removal of all unsound and potentially dangerous material. In general, dry hydration to powder produces a material of much coarser grain and less plastic in properties, than slaking in an excess of water to a putty. Dry hydrated lime must be distinguished from ground quicklime, which, when made by grinding a high calcium lime, may be dangerous to transport or store, owing to risk of fire from accidental access of moisture.

Properties and Use.

Type 1. High Calcium.—These limes are rapid-slaking, with large evolution of heat, and afford a high "volume yield" (volume of lime putty of a certain fixed consistence per unit weight of quicklime taken). They are usually "plastic" in the plasterer's sense, the Mountain type more so than the Cretaceous. Being non-hydraulic, "setting" of a high calcium lime mortar or plaster is by drying only, and when continuously moist such limes never "set," so that they are unsuitable for use in damp situations. Any hardening is by a slow process of absorption of atmospheric carbon

dioxide, which penetrates extremely slowly into the mass and depends on a favourable degree of moisture as well as on free access of air. Under favourable conditions, in time a considerable degree of strength can be attained, and in their own districts high calcium limes will be preferred to any other for building purposes, and even used in preference to Portland cement mortar in high walls.

For "chemical" uses the high calcium lime will almost always be preferred.

Type 2. Moderately Hydraulic.—These comprise mainly the "greystone" limes of the Thames basin. They are generally quick-slaking, and give a fair "volume-yield" of putty and a workability comparable with that of a white chalk lime. As usually employed for plastering in the south of England, they are run to putty and stored in this condition for some weeks before use, in which case a large proportion of the hydraulicity has naturally vanished by the time they are used; but if used as soon as may be safe and practicable after slaking, or as a dry hydrated product which is merely mixed with water and employed like cement without delay, they exhibit a very useful degree of hydraulicity, setting out of contact with air and in a damp situation. The set is slow, three months being required for the development of a large proportion of the ultimate strength.

Type 3. Eminently Hydraulic.—The British eminently hydraulic limes vary widely in properties, and require correspondingly different treatments when employed for their principal purpose, namely as mortar limes for building. Unlike the corresponding products on the Continent, they are usually marketed in an unslaked condition, often as "ground lime," and any further preparation for use has to be made on the building site, often by unskilled labour. Such slaking as is carried out here on the site is only a crude version of the highly developed processes employed on the Continent for preparing their eminently hydraulic limes, viz., alternate crushing, watering, storage in silos or huge piles, sifting, light crushing, etc., etc. By the latter named methods two or three products, of varying degree of hydraulicity, are prepared from the same material, all non-expansive and sound, and the slow-slaking "grappiers" are separated.

Type 3 (*a*), Liassic, may be rapid-slaking (almost explosively so in fine powder form) and showing a large expansion in the process. Some varieties can be slaked to a putty, but the usual method is to dry hydrate the lump quicklime in a large pile, cover with sand and leave for 24–48 hours to heat up and steam before mixing with more water and sand for use.

Types 3 (*b*) and 3 (*c*) may contain so little free lime that they will be described as "non-slaking," and are then used (as ground quicklime) just as if they were Portland cement: any expansion must take place before the mortar has hardened if trouble is to be avoided. Some show a flash set, due to the rapid adsorption of the mixing water by the unslaked lime. Eminently hydraulic limes, in general, usually harden somewhat more rapidly than the moderately hydraulic, type 2, but more slowly than Portland cement.

Type 4. Magnesian.—The British magnesian limes are slow-slaking, and generally not all of the magnesium oxide present will hydrate to magnesium hydroxide, $Mg(OH)_2$, under conditions adequate completely to hydrate the lime: accordingly there is a danger that unless very thoroughly slaked they may contain slow-slaking particles which will slowly expand (by slaking) in the finished work, and produce symptoms of unsoundness. They are employed mainly as mortar limes, and are, quite justly, greatly valued as such in their own territory, where the knowledge of their correct treatment is traditional. For mortar they are preferably slaked as type 3 (*a*) above. A. D. C.

IV. Magnesium Oxychloride Cement.

Magnesium oxychloride cement ("magnesian cement") was first described by Sorel [1] in 1867. The commercial applications of the material were soon realised and it is now widely used as a building material, chiefly in the manufacture of patent "composition" floors and wall-coverings

When magnesium oxide, prepared by calcining the carbonate at a moderate temperature (about 700°C. to 1,000°C.), is made into a paste with a strong solution of magnesium chloride, the mass sets forming a hard, strong cement. The reaction has been the subject of many investigations, and it is now generally accepted that the setting of the cement is due to the formation of hydrated magnesium oxychloride, although the exact composition of the latter is still somewhat uncertain.

Bender,[2] examining the set cement after it had been exposed for 6 months in the air, found it to consist of a mixture of $MgCO_3$ with $5MgO,MgCl_2,17H_2O$. By prolonged treatment with water the whole of the magnesium chloride was extracted, leaving a compact, hard residue of $2MgO,3H_2O$.

Kallauner [3] advanced the view that the cement is a solid solution and not a definite compound.

Lukens [4] studied the reaction between $MgCl_2$ solutions and MgO obtained by igniting $Mg(OH)_2$ and found that the oxide dissolves in the solution of the chloride with subsequent precipitation of a compound corresponding to the formula $5MgO{\cdot}MgCl_2,xH_2O$. This compound, on continued treatment with magnesium chloride solution of specific gravity greater than 1·16, is converted into $3MgO{\cdot}MgCl_2{\cdot}7H_2O$.

Bury and Davies [5] studied the system $MgO-MgCl_2$—water, previously investigated by Robinson and Waggaman [6] and Maeda and Yamane.[7] At 25°C., the solid phase co-existing with dilute solutions of the chloride was found to be $Mg(OH)_2$. Gels were formed at 25°C. when the concentration of $MgCl_2-H_2O$ was 9·7% or more. The nearest formula for the oxychloride was $10MgO{\cdot}3MgCl_2,35H_2O$ or $3MgO{\cdot}MgCl_2,11H_2O$. The latter was only stable in contact with solutions containing 10·9% or more of $MgCl_2$, and was not formed spontaneously on either MgO or $Mg(OH)_2$ by solutions containing less than 13% $MgCl_2$.

A typical pure magnesium cement, containing no filler, was found to contain 43% MgO, 12% $MgCl_2$, and 45% H_2O. In a cement containing fillers as used in practice the proportion of $MgCl_2$ would be higher. At 25°C. the cement is composed of three phases, hydroxide, oxychloride, and a 10·9% solution of $MgCl_2$. The latter liquid constitutes 10–14% of the mass; thus, although the set cement is hard, it must be porous. The cement is unstable when exposed to the atmosphere, the $Mg(OH)_2$ becomes carbonated, and the 10·9% solution of $MgCl_2$ will adsorb moisture if the atmospheric humidity exceeds 93%. Adsorption of moisture decomposes the oxychloride, ultimately converting the cement into $Mg(OH)_2$ and a dilute solution of $MgCl_2$. In practice, disintegration from this cause is reduced as the result of carbonation, and also by the customary treatment of the surface with oil or wax.

Chassevent[8] found that the setting of magnesium oxychloride cement consists essentially in the precipitation of a supersaturated solution of magnesia in magnesium chloride solution. The total quantity of MgO dissolved before setting commences is dependent upon the concentration of the $MgCl_2$ solution, after the latter exceeds 10%, the rate of precipitation increases rapidly and becomes very marked when the concentration is higher than 30%. Those solutions which yield the greatest amount of supersaturation are those which lead to the earliest development of high compressive strength. Magnesium hydroxide dissolves only very slowly in $MgCl_2$ solutions, and this accounts for its slow setting and feeble hardening.

Free lime, which is present to varying extents in commercial samples of magnesia, may exert a deleterious effect on the cement, causing expansion and weakening.[9, 10, 11]

Other chlorides, e.g. $CaCl_2$ and $FeCl_2$, can be substituted for $MgCl_2$ and under suitable conditions are capable of giving strong cements. Dolomite, calcined below the dissociation temperature of $CaCO_3$, can form strong cements with either $MgCl_2$ or $CaCl_2$.[12] Canadian magnesitic dolomite has been used successfully in producing magnesia suitable for flooring work.[13]

Magnesia of the type used in the manufacture of the cement is described as "caustic" or "plastic" magnesia, in distinction from the "dead burnt" magnesia (relatively inert towards $MgCl_2$) which is used for refractories and other purposes.

The caustic magnesia used in England is obtained chiefly from Grecian and Indian magnesites; in these, the content of calcium and iron compounds and other impurities is usually low. The chemical purity of a sample, however, is not in itself a criterion of the suitability of the material for use in cement work, since the active properties are largely controlled by various factors in the calcination process, and by the fineness of grinding of the product.[10] They may also be affected by subsequent exposure of the magnesia to air.[10, 12]

It is necessary, therefore, in selecting a sample of caustic magnesia, to take into account not only its chemical analysis, but also the properties of the cement it will produce, e.g. the setting time, strength, and volume constancy. It is important for a flooring contractor to be sure of obtaining supplies of magnesite of constant properties.

A useful characteristic of magnesium oxychloride cement is its strong cementitious action towards fibrous organic fillers such as sawdust, as well as sand and other inorganic aggregates. The action is maintained even when the magnesia is diluted with several times its own volume of filler. The fillers most commonly employed in practice are sawdust, wood flour, and asbestos fibre together with a smaller proportion of finer material such as talc, ground silica, or barytes.

The composition of mixes can be varied widely according to the type of product required. Floors and wall-coverings are often laid in two coats, the first containing a high proportion of coarse fibrous fillers (e.g. 3 to 4 volumes of sawdust to 1 volume of magnesia), while the finishing coat is made up with finer material (e.g. 2½ volumes of wood flour and a little talc or asbestos fibre to 1 volume of magnesia) to facilitate the production of a dense, hard, polished finish. Hard wearing factory floors are sometimes made with inorganic fillers only. Mixes made with coarse and fine sand have been used for external stucco work in the U.S.A.[4] Similar hard aggregates are used in preparing pre cast flooring tiles, table-tops, etc.

The most suitable pigments are those of the permanent type, such as the earth colours and chromic oxide.

Both pigments and fillers should be inert towards the active ingredients of the cement, they should contain no free lime, and their content of water-soluble matter should be low.

The magnesium chloride solution used for "gauging" the dry ingredients of the mixture is prepared by dissolving the commercial "fused lump" or flakes in water. The strong solution is diluted to the requisite specific gravity, this being usually quoted on the Baumé or the Twaddell scale. Some latitude is permissible in the strength of the solution, but 20° to 23° Bé (sp. gr. 1·16 to 1·19) is suitable for most mixes.

The mixture is "gauged" with the minimum amount of solution necessary to produce a working consistence, avoiding any excess, since this is liable to prove deleterious to the product. The background on which the cement is to be laid is first moistened and the mass then placed thereon and compacted thoroughly. The setting-time varies considerably with different mixes and conditions, but setting is usually complete within 24 hours. When the finishing coat has been laid, a smooth surface is produced by scraping, trowelling, washing with a weak solution of the chloride, and scrubbing with fine steel wool. The surface when hard and dry is finally treated with oil or wax.

Certain precautions are necessary when laying oxychloride cement in buildings. The chloride solution is liable to cause corrosion in iron and steel work; hence the latter must be protected. Iron pipes passing directly through the cement should be carried through sleeves. Structural

steel, service pipes, conduits, etc., lying beneath the cement should be coated with a protective paint. Cases have been known in which chloride, finding its way through porous or cracked concrete, and so into contact with unprotected steel joists, has caused extensive damage.

It is necessary to prevent the adsorption of chloride by neighbouring floors and walls, since it is likely to give rise to permanently damp patches. Plaster-work adjacent to oxychloride cement work should be insulated by means of fillets.

The possibility of subsequent movement and cracking of the cement will be minimised if the surface of the background is well roughened so as to provide an adequate "key." When roughening is impracticable, as in the case of wooden or steel sub-floors, some form of artificial anchorage should be provided. When the cement is laid over large areas, it is advisable to provide one or more "expansion" joints.

In its chief use, *i.e.* as a flooring material, magnesium oxychloride cement possesses advantages in respect of appearance, warmth, lightness, and resilience, combined with high strength. During recent years there appears to have been some lack of care and discrimination in the use of the material in certain cases, and troubles due to cracking, swelling, or "sweating" of floors, and corrosion of steelwork have sometimes been experienced. Where proper control is exercised in the processes of manufacture and laying, such defects should not occur.

West, Sebastian, and Darrow give a Bibliography of Magnesian Cements [14] comprising 211 classified references.

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H. M. L.

V. Natural Stones.

Many varieties of rock have been used as building stone. Domestic and ecclesiastical buildings frequently reflect the nature of the country rocks, but where supplies of suitable materials were lacking, stone was carried long distances even in early times. With modern transport facilities choice can be founded on suitability, æsthetic considerations, or fashion rather than on accessibility.

Building stones can be broadly classified as:

(*a*) Granites.
(*b*) Limestones.
(*c*) Marbles.
(*d*) Sandstones and grits.
(*e*) Slates.

Details regarding individual varieties may be found in the works of Watson and others, cited below.

Granites are rocks of igneous origin consisting of dense aggregates of interlocking crystals of quartz and various silicate minerals (felspar, mica, hornblende, augite, etc.). A wide range of textures and colours is available. The many other varieties of igneous rock recognised and classified by geologists are not so widely distributed as the granites and, except locally, they are less commonly used for building. An exception is the iridescent augite-syenite from the Laurvik district of Norway, familiar in Great Britain as dark, light, or emerald pearl. In commerce the term "granite" is often incorrectly applied to any type of igneous rock, and even to hard rocks not of igneous origin. "Mendip Granite," for instance, and the "Petit Granit" of Belgium are both limestones.

Limestones and marbles consist essentially of crystalline calcium carbonate, usually in the form of calcite. Magnesium carbonate commonly occurs in small amounts. In the magnesian limestones it occurs in more or less equimolecular proportions with calcium carbonate. Limestones are sedimentary rocks. Strictly, a marble is the product of metamorphism of a limestone, but in commerce any limestone that will take a polish is commonly described as marble. Many varieties of structure are met with among limestones. They may be hard, dense rocks like those commonly met with in England in the Carboniferous and Devonian deposits or they may be relatively soft and porous like those of the Jurassic and Cretaceous deposits. In Great Britain the Jurassic rocks have furnished the more widely used varieties of limestone. Their essential qualities depend on physical structure rather than on chemical composition.

Sandstones and grits consist essentially of grains of quartz, with felspar, mica, and other mineral residues from the igneous rocks of which they are the sedimentary degradation products. The term "grit" is applied to the coarser varieties of sandstone. The mineral grains may be angular or more or less rounded. They are generally united with a cementitious material which may be siliceous, ferruginous, calcareous, or argillaceous in character. The grains may be relatively sparsely scattered in the secondary cement, or they may be closely packed, with but

small amounts of intergranular material. In the rare deposits of "flexible sandstone" found in India and Brazil there is no cementitious binding material; the cohesion of the rock depends on an interlocking of the individual grains.

Slate is a metamorphic rock. Its essential character is that it can be split in a direction which is independent of the bedding of the fine-grained sedimentary strata from which it originated. Numerous minerals are usually recognisable; some, original grains present in the parent rock; some, secondary products of metamorphism. The fissile character of slate is due to an orientation of tabular minerals such as mica in planes perpendicular to the direction of the earth pressure which contributed to its formation A few varieties of fissile sedimentary rock, which are not true slates because they cannot be split except along the bedding planes, have been used as roofing materials. Examples are the stone tiles of Stonesfield and Collyweston.

Flint, serpentine, soapstone, or potstone, laterite, and other miscellaneous rocks have been used locally as building stone. Each of these is considered under its respective heading.

The structures of building stones can be conveniently studied in thin section under the microscope. Impregnation with synthetic resins facilitates the preparation of sections of soft and friable materials, and if the resin is suitably coloured the method is of assistance in the study and classification of structures.

Causes of Decay.

There is abundant evidence in old buildings that good stone, properly used, is a very durable material. But, like the rocks in nature, building stones are subject to the action of agents of weathering and decay. The causes of weathering are many No one agent can be made the scapegoat for all decay. Broadly speaking, it may be said that coarse-textured igneous rocks are detrimentally affected by temperature changes; that calcareous materials are susceptible in varying degrees to attack by water carrying in solution carbon dioxide and acid sulphur gases derived from coal smoke; and that all porous stones are more or less readily damaged by soluble salts. Stone may also become seriously decayed by faulty handling, by ill-judged choice or association of materials, or by ill-advised methods of treatment; such technical errors which may bring a good stone into disrepute, may, however, be avoided.

Because the minerals present have different coefficients of expansion repeated alternations of temperature cause a loosening of the structure of granites and similar rocks, and, in time, possibly by the action of frost on the fissured material, the exposed surfaces become very friable. A temperature effect of a grosser kind, which may affect any type of building stone, is the severe cracking and spalling that occurs if long lengths of masonry are fixed without expansion joints between massive abutments. Frost, another thermal agent, is only effective in the presence of moisture. Except with argillaceous materials and with those porous materials which by virtue of their structural characteristics become very highly saturated by rain, frost is believed to be a relatively unimportant primary cause of decay in Great Britain, though it may often have some contributory effect when the stone has been weakened by other causes. Measurement of the saturation coefficient

$$\left(\text{ratio } \frac{\text{water absorption by volume}}{\text{total porosity}}\right),$$

a term due to Hirschwald, is a useful criterion of frost resistance. But even stones with high saturation coefficients are seldom seriously affected by frost except in copings and similarly exposed situations. Measurement of the saturation coefficient of porous limestones often affords an indication of general durability, but this does not imply that frost is always a major cause of decay. The reason is that both durability and saturation coefficient are dependent on structure.

Pollution of the atmosphere by coal smoke—much of it of domestic origin—is responsible for disfiguration by soot deposits, and decay due to the chemical action of acid sulphur gases forming calcium and magnesium sulphates in limestones and other calcareous materials Pollution products are widely distributed by clouds and wind, and their effects are often apparent in districts far removed from centres of population.

Contamination by soluble salts other than those formed by atmospheric agencies is a common and avoidable cause of decay. Alkali salts also cause staining of limestones. Soluble salts may originate in various sources including the soil, brick and concrete backing materials, jointing materials, and chemical cleaning agents Decay of limestone frequently follows contact with sea water, but although the air of seaside towns contains appreciable amounts of chlorides the condition of ancient buildings on the coast demonstrates that chlorides are not adsorbed from the air in sufficient quantities to exercise seriously detrimental effects Soluble salts frequently appear on the surface as efflorescent deposits the composition of which varies considerably according to their origin. Sulphates and carbonates of sodium, and magnesium sulphate, commonly occur. Contrary to common belief calcium sulphate is rarely a major constituent of efflorescences.

Contamination with soluble salts may cause very serious disfiguration and ruin stone of the highest quality. Every effort should be made to avoid it. Soil moisture and salts may be adsorbed through ineffective damp proof courses Paving is sometimes laid above the level of the damp-proof course; splashing may introduce salts above the damp proof course. For these reasons the use of granite of good quality in base courses has much to recommend it. Where masonry is laid in contact with brick backing it is an advantage to apply a bituminous paint to the back of the stone; a slurry of lime or cement is useless for the purpose. It is also desirable with permeable stones to cover cornices and string courses with lead flashing to prevent excessive penetration of rain water to the backing materials. Marble linings should

be fixed with plaster of Paris. Portland cement and Keene's cement provide soluble salts and should not be used. As a further precaution to avoid contamination from the backing materials, the back of the marble, including the dowel holes, should be treated with shellac. The use of alkalis or other chemical agents for cleaning stone should be avoided as such use is a common cause of salt contamination.

In the presence of calcium sulphate or other soluble salts the use of dense mortars which limit evaporation through the joints may accentuate decay in the adjacent stone. Ancient buildings have often been damaged by injudicious repointing. Mortars rich in Portland cement should be avoided and the mortar should not be excessively trowelled; a brushed finish is preferable.

Lichens occasionally cause pitting of the stone surfaces on which they grow, but their action is seldom important. They are not found where the atmosphere is heavily polluted by coal smoke. Ivy is detrimental particularly to ruined structures where the aerial roots can gain foothold in the joints. In spite of prolonged researches no convincing evidence has yet been adduced to show that micro-organisms play any significant part as causative agents of decay.

Choice and Testing of Building Stone.

Custom, ready availability in the sizes required, and cost are often controlling factors in the choice of building stone. Questions of colour, texture and ease of working need consideration. Durability is generally important. Often in stone selected for carving, durability is sacrificed for uniformity and appearance. Wide variations in quality are found within each group of materials. Different strata in a quarry may have widely different properties, and the quarryman's claims to be able to differentiate between good stone and bad are not always substantiated by events. The examination of existing buildings often provides valuable information as a guide in selection of stone, but the information so obtained can often be usefully supplemented by the application of laboratory tests. The quality of a stone can be assessed by means of relatively simple tests, the nature of which depends upon the character of the stone. Crushing strength is not a criterion of quality. Chemical analysis affords little help. Microscopical examination is useful, particularly in classifying different types of structure, but further practical tests are usually required. Simple acid immersion tests, crystallisation tests, and tests depending on measurements of the capillary characteristics of porous materials are valuable. With all tests of this kind it is essential that an adequate range of information on samples of known quality from buildings should be available as a basis for interpretation. When small quantities of stone are required for monumental purposes it is practicable to test each block. For work on a larger scale the most satisfactory procedure is to sample the quarry systematically. Tests can then be applied to ascertain what range of quality is likely to be encountered. The most durable seams may then be located and visible characteristics of the stone of good and inferior quality may sometimes be noted to serve as a guide in selection.

Restoration, Preservation and Cleaning.

The restoration of old masonry can be carried out by replacement with new stone or by rebuilding defective parts with a plastic material. If new stone is used it is important to choose material of a similar kind to that in the building: limestone should be repaired with limestone, sandstone with sandstone. Magnesian limestones present special difficulties owing to the formation of highly soluble magnesium sulphate on weathering. The execution of plastic repairs is a skilled operation. Work of this character should either be placed in the hands of a specialist firm or should be carried out under experienced supervision. It is very important that the repairs should be securely keyed into the stone by undercutting, and, where necessary, by provision of dowels of non-corrosive metal. "Feather-edging" should be avoided. Furthermore, plastic repairs should be substantial: the application of thin renderings over slightly eroded stone is a misuse of the method of repair and is never satisfactory.

Various materials have been employed as "stone preservatives" with the object of waterproofing or hardening the stone, but in general the results, extending over the past 75 years, have been disappointing. It cannot be too forcibly stated that good stone does not need preservative. Recognition of this rule would save much unnecessary expense. A good oil paint applied to a surface in sound condition when the stone is suitably dry has very good protective properties, but it needs renewal every few years. The use of paint for this purpose is often objectionable on account of its appearance. The protective power of colourless stone preservatives is very definitely less than that of paint, and such materials need renewal even more frequently. Their effect on appearance is apt to be objectionable and there is often a danger that ultimately the treated surface may flake off. Where decay is associated with the presence of efflorescent salts surface treatment of any kind is unquestionably useless.

For the treatment of stone contaminated with soluble salts washing with water to remove the salts is the only method that can safely be employed. Steps should first be taken to ascertain the origin of the salts and to take such measures as may be found necessary to remedy any defects that may be present. Excessive water penetration through copings, sills, string courses, and similar catchment surfaces, and adsorption of soil moisture through defective damp-proof courses are common causes of efflorescence that can be remedied. The surface should then be brushed to remove salts and loose particles, and, after removing any accumulation of debris from the foot of the wall, the surface should be washed with plenty of clean water. The brushing and washing need to be repeated as long as salts continue to reappear as the stone dries.

Periodical washing is a useful method of maintenance of stone buildings. Very dirty

buildings can be cleaned by scrubbing with bristle brushes assisted by a jet of water or steam. Sometimes it is necessary to scour the surface with gritstone or carborundum, a practice which is not necessarily harmful to the stone. The alleged development of a protective skin due to the drying out of the quarry sap has little foundation in fact. The hard, discoloured skin which is usually present in sheltered places, especially on limestones, consists largely of calcium sulphate and is not protective.

With the exception that the use of ammonia is permissible for the removal of green copper stains, chemicals should not be used for cleaning stone The use of acids or alkalis to facilitate cleaning commonly causes serious subsequent decay Reputable firms engaged in stone cleaning and restoration are prepared to guarantee that chemicals will not be used, and it is inadvisable to employ any process for which the operators are not prepared to give this guarantee. Weather stains which cannot be removed by water or steam should be allowed to remain.

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VI PORTLAND AND OTHER HYDRAULIC CEMENTS AND CONCRETES [1]

Portland Cement.

This is by far the most important constructional cement and its world production exceeds 70,000,000 tons per annum Its invention is usually attributed to Joseph Aspdin, of Leeds, who took out a patent in 1824. Isaac Johnson, however, claimed to have been the first to suggest firing at a sufficient temperature to produce vitrification The name was given to the material on account of some resemblance in colour of the set product to Portland stone

Composition.

Portland cement is composed of lime, silica, alumina, and ferric oxide together with small amounts of magnesia, titania, and alkalis. A few per cent. of gypsum are also added during grinding to control the set of the product. A typical analysis is as follows:

	%
CaO	64 4
SiO_2	21·2
Al_2O_3	5 4
Fe_2O_3	3 3
TiO_2	0 2
MgO	0 8
Na_2O	0 4
K_2O	0 6
SO_3	2 3
H_2O and CO_2	1 4
	100 0

[1] In this section the word "cement" is used to mean a calcareous compound employed in building and does not refer to adhesives such as glue

Appreciable variations from the above values may occur and the ranges which the various constituents may show are about: CaO 60–67%, SiO_2 17–25%, Al_2O_3 3–8%, Fe_2O_3 2–6% (dropping as low as 0·5% in white Portland cement), MgO 0·1–5·5%, Na_2O+K_2O 0·5–1·5%, SO_3 1–3%.

The limits laid down by the British Standard Specification are as follows: The molecular ratio of lime (after deduction of the proportion necessary to combine with the sulphur trioxide present) to silica plus alumina shall not exceed 3·0 nor be less than 2·0. This ratio

$$\frac{CaO}{SiO_2+Al_2O_3}$$

is called the British hydraulic modulus. The content of magnesia shall not exceed 4%, that of sulphur trioxide 2·75%, the ignition loss 3% (4% for hot climates). The content of matter insoluble in dilute acid shall not exceed 1·0%.

Portland cement is formed by a clinkering process in which the raw materials are heated to a temperature such that only a portion, some 20–30%, of the mix, is melted. Much work has been carried out to determine the nature of the compounds formed and the constitution is now fairly clear. Studies on the phase equilibria in the systems $CaO–Al_2O_3–SiO_3$ (Rankin and Wright, Amer. J. Sci. 1915, **39**, 1), $CaO–Al_2O_3–Fe_2O_3$ (Hansen, Brownmiller, and Bogue, J. Amer. Chem. Soc. 1928, **50**, 396), $CaO–Al_2O_3–SiO_2–Fe_2O_3$ (Lea and Parker, Phil. Trans. 1934 (A), **234**, No. 231, 1; Lea, Cement, 1935, **8**, 29), have shown that the compounds formed from lime, alumina, silica, ferric oxide, in Portland cement clinker are $3CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$, $3CaO{\cdot}Al_2O_3$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, and sometimes $5CaO{\cdot}3Al_2O_3$. The magnesia is present in part, and perhaps entirely, as the free oxide. Little is definitely known of the mode of combination of the alkalis and titania. A certain amount of glass may also be present owing to the failure of the liquid formed during clinkering to crystallise completely on cooling.

Most cements contain a small amount of uncombined lime due to incomplete combination in burning. The content may vary from 0–5%. The larger proportion of this is usually converted to the hydroxide during grinding of the cement by combination with water derived from the added gypsum. The minerals which could be identified in Portland cement were formerly called alite, belite, celite, and felite before their composition was known. Alite is tricalcium silicate, belite and felite are both forms of dicalcium silicate, while the celite is probably to be identified as tetracalcium aluminoferrite.

Tricalcium silicate has all the essential cementing qualities of Portland cement. The ground material sets in a few hours and develops strength rapidly. Dicalcium silicate sets only very slowly over several days and does not develop appreciable strengths until after 28 days. The strength progressively increases with age and after a year or more equals that of tricalcium silicate. Tricalcium aluminate gives an almost instantaneous set with water and develops much heat. Addition of gypsum or lime retards the set somewhat. The compound $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ also sets rapidly, though less so than tricalcium aluminate. The extent to which these two compounds contribute to the strength of Portland cement is uncertain, but it seems that tricalcium aluminate may make a contribution to the strength developed over the first few days.

When Portland cement reacts with water at ordinary temperatures the silicate compounds liberate calcium hydroxide and form a less basic hydrated calcium silicate of formula $xCaO{\cdot}SiO_2$ aq. where the value of x is probably 1·5 or 2. Hydrated silicates of both these $CaO:SiO_2$ ratios exist. The tricalcium aluminate on hydration forms either a hydrated tricalcium or tetracalcium aluminate. The latter is formed by combination with the calcium hydroxide liberated from the silicates. The hydrated tricalcium aluminate combines with the gypsum present to form calcium sulphoaluminate:

$$3CaO{\cdot}Al_2O_3+Aq.=3CaO{\cdot}Al_2O_3.\ aq.$$
$$3CaO{\cdot}Al_2O_3.\ aq.+CaSO_4,2H_2O+aq.$$
$$=3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4,31H_2O$$
$$3CaO{\cdot}Al_2O_3+Ca(OH)_2+12{\cdot}5H_2O$$
$$=4CaO{\cdot}Al_2O_3,13{\cdot}5H_2O$$

At least three different hydrated tricalcium aluminates exist:

$3CaO{\cdot}Al_2O_3,6H_2O$ (cubic),
$3CaO{\cdot}Al_2O_3,12H_2O$ (hexagonal),
and $3CaO{\cdot}Al_2O_3,18H_2O$ (probably orthorhombic).

The compound $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ possibly forms hydrated tricalcium aluminate and a hydrated mono-calcium ferrite, but other hydrated calcium ferrites exist and may be formed in set cement.

The hydration of Portland cement is a surface action and proceeds only slowly into the interior of the individual grains. The depth of hydration is less than 10μ after six months, and the coarser particles probably never hydrate completely. On regrinding an aged set cement the reground material will set and harden again owing to the unhydrated material present.

Two alternative theories have been propounded to explain the setting of cement. The "crystalline" theory of Le Chatelier attributes the hardening to the interlocking of crystals formed during hydration, as in the setting of plaster of Paris. In the "colloidal" theory of Michaelis it is considered that the hydration products of the silicates at least are formed as rigid gels, and the development of strength is due to the hardening of the gel. This theory appears the most satisfactory, since at ordinary temperatures the hydrated calcium silicates appear to be non-crystalline, and, further, certain physical properties of set cement are most readily explained on the gel theory. It is, however, often argued that the gel is really microcrystalline and that the two theories are not incompatible.

Set cement when it dries for the first time undergoes an irreversible shrinkage and also shows an irreversible change in its vapour pressure—water content curve similar to that

shown by silica gel. On subsequent cycles of wetting and drying there occurs a reversible volume change which is less in magnitude than the first irreversible movement.

The hydration of Portland cement is accompanied by a marked heat evolution which causes a considerable rise in temperature in the interior of large concrete masses. The tricalcium aluminate contributes most to this heat evolution, tricalcium silicate next, and tetracalcium alumino-ferrite and dicalcium silicate the least. The heat evolution mostly occurs over the first seven days of hardening and varies from about 40–90 g. cal. per g. at 7 days for different Portland cements.

Manufacture.

As would be anticipated from the composition of Portland cement it can be prepared from raw materials of various sorts. Chalk, limestone or any other suitable form of calcium carbonate can be used as the source of lime, while the alumina and silica may be derived from clays or shales. Materials containing both calcareous and argillaceous constituents such as marls, argillaceous limestones, and calcareous shales can similarly be used. Blast-furnace slag and alkali-waste are also used. Minor additions of ground sand are also sometimes made when the silica SiO_2/R_2O_3 ratio of the clay is low. In general the manufacture of Portland cement can be undertaken at any place where suitable deposits of raw materials occur and the cost of fuel is not too high. Certain raw materials, however, because of ease of handling or of grinding and mixing, have advantages. Thus the chalk and river mud of the Thames and Medway, being soft materials which were easily handled and mixed, attracted the cement industry to that district in the first instance. In the United States of America the industry was first established in Pennsylvania where argillaceous limestones approximating in composition to Portland cement, and requiring only small additions of limestone to correct the composition, were available. With the greatly increased efficiency of modern grinding mills, hard raw materials such as carboniferous limestones and hard shales can be handled and properly mixed: materials of these types are now used at many cement plants.

The following are analyses of some of the raw materials commonly employed:

Chalk.

	%
Moisture	19·03
Sand and clay	0·93
Combined silica (SiO_2)	0·43
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	0·48
Lime (CaO)[1]	42·90
Magnesia (MgO)	0·42
Carbon dioxide (CO_2)	34·16
Alkalis, organic matter, and loss	1·65
	100·00

[1] Corresponding with calcium carbonate ($CaCO_3$) 76·60 p.c.

Clay.

	%
Sand	28·42
Combined silica (SiO_2)	30·32
Alumina (Al_2O_3)	15·49
Ferric oxide (Fe_2O_3)	7·74
Lime (CaO)	2·04
Magnesia (MgO)	1·96
Sulphuric anhydride (SO_3)	1·96
Combined water and loss	12·07
	100·00

Limestone.

	%
Insoluble silicious matter	0·20
Alumina+ferric oxide ($Al_2O_3+Fe_2O_3$)	0·08
Lime (CaO)	56·02
Magnesia (MgO)	0·24
Carbon dioxide (CO_2)	43·38
Combined water and loss	0·18
	100·10

Shale.

	%
Silica (SiO_2)	60·22
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	27·20
Lime (CaO)	trace
Magnesia (MgO)	1·62
Carbon dioxide+water (CO_2+H_2O)	4·54
Alkalis and loss	6·42
	100·00

Marl.

	%
Silica (SiO_2)	15·10
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	7·30
Lime (CaO)	42·16
Magnesia (MgO)	0·34
Carbon dioxide (CO_2)	33·51
Water, alkalis, and loss	1·59
	100·00

Whatever the nature of the raw materials the first step in the manufacture of Portland cement is to secure their comminution and intimate admixture. This is of primary importance, since in burning cement the materials are only clinkered and not fused and coarse particles fail to combine completely. The fineness to which the raw materials are ground varies from 1–10% residue on a 170 B.S. mesh sieve depending on the nature of the materials to be mixed.

There are two processes of manufacture known as the "wet" and the "dry" process. In the wet process the raw materials are ground with water to a slurry containing from 35 to 50% water and this slurry is fed to the kilns. Slurry filters are sometimes used, mainly in the U.S.A., and the resulting wet coke fed to the kiln. It contains from 20 to 30% water. In the dry process the raw materials are dried, and ground to a fine powder, and fed to the kiln in this condition. The wet process has always been favoured in Great Britain, but the dry process

was formerly favoured in the United States of America and elsewhere. Certain raw materials such as chalk and clay are most easily treated by the wet process, but for rock materials the dry process offers some advantages. As, however, the wet process renders possible a more accurate control of the raw mix than the dry process it is now widely used for all types of raw materials.

The procedure in the wet process varies with the nature of the raw materials. In the case of soft, wet materials such as chalk and clay the two substances are mixed in the required proportions into a wash mill, which is a large tank in which revolves a vertical spindle having radial arms from which hang harrows. Water is added to give the required fluidity to the slurry. The slurry passes through screens which retain stones and grit, and is then further ground by treatment in another wash mill with finer screens, in centrifugal screening mills, or in a tube mill. The tube mill is a steel cylinder rotating on its axis and containing a charge of steel balls or cylinders, or other grinding media. It is often divided into several compartments containing balls of different sizes. The material to be ground enters at one end, passes down the cylinder and out at the other end. It is ground by the steel balls which are continually raised up the periphery of the cylinder and continually drop back on to the materials being ground. After being ground the slurry is pumped to slurry basins or storage tanks in which both rotating arms and agitation by compressed air are used to keep the mixture homogeneous. The composition of the slurry is checked by analysis and corrected by suitable blending with other tanks, or by adjustment of the charge being fed to the wash mills.

Other methods of preparation of the slurry are used when dealing with harder raw materials. Such materials are crushed dry and then fed in the required proportions to a tube mill to which water is added in the amount required to form the slurry.

The burning of Portland cement was formerly carried out in various forms of shaft and chamber kilns, but these have been superseded almost entirely by the rotary kiln (Fig. 1). This is a long steel cylinder rotating on its axis and slightly inclined so that the materials fed at the upper end travel slowly to the lower end. It is lined with refractory bricks, and is fired at the lower end with pulverised coal, or oil, or gas where economical to do so. The fuel is blown

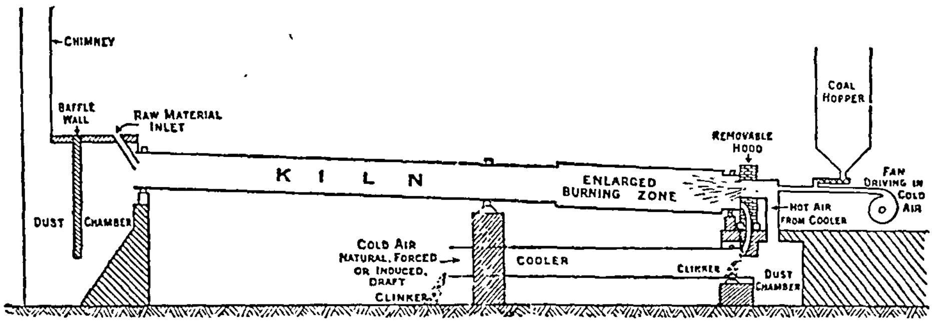


FIG. 1.

in from a jet by compressed air and the flame projected up the kiln somewhat like a blowpipe flame. Chains are often fixed inside the kiln at its cold end to lift the raw materials as the kiln rotates and so facilitate the interchange of heat from the hot gases. The raw mix is first dried as it passes down the kiln; it then enters a zone where decarbonation takes place and combination begins and finally reaches the clinkering zone, close to the firing end. Here the raw mix attains a temperature of 1,300°–1,500°C. and combination is completed. The clinker issues from the kiln as small, dark, rounded particles varying in size from a pea to a walnut. After leaving the kiln the clinker passes into coolers. In older plants these consist of rotating steel cylinders arranged usually underneath the rotary kilns, but in most modern plants they form a composite part of the kiln. In such cases they consist of a series of cylindrical tubes parallel with the body of the kiln and arranged circumferentially around the outlet end of the kiln. Air is drawn through the coolers and then used for the combustion of the fuel, so leading to an economy in heat. In dry process plants steam boilers are often installed to utilise the waste heat from the exit gases. This is done in occasional instances also in wet process plants. The dimensions of rotary kilns vary from some 150 ft. long and 9 ft. internal diameter in many dry process kilns to 200–300 ft. long and up to 11 ft. diameter for most wet process kilns. Recently rotary kilns have been built with a length exceeding 500 ft. having an output approaching 4,000 tons per week.

The clinker is carried by conveyors to the grinding mills or to storage piles. Grinding is usually carried out in tube mills to which the clinker is fed together with the amount of rock gypsum required to control the setting time of the cement. The ground cement is stored in silos from which it is fed to automatic packing machines.

Testing Portland Cement.

The quality of cement is ascertained by various mechanical tests and by its chemical composition. The limits placed in the composition (*see* earlier) are such as to ensure that the material is, in fact, a Portland cement, and that the amounts of magnesia and sulphur trioxide present are not such as to endanger the quality of the product. Excessive contents of these constituents may cause the cement to

be unsound and concrete containing it to expand and disrupt after hardening The physical and mechanical tests laid down in the British Standard Specifications (1931) are as follows.

Fineness.—The residue on a British Standard mesh sieve 170×170 must not exceed 10%, and that on a 72×72 mesh 1%.

Consistence Test.—The amount of water to be used in gauging the cement mortar for the tensile briquettes, and the neat cement for the setting time and soundness tests, is obtained from a consistence test on the neat cement. The neat cement is gauged with water and the percentage found by trial such that a Vicat plunger (a cylindrical rod, 300 g weight, 1 cm. diameter, with flat lower end) released at the surface of a mould filled to a depth of 40 mm. with cement paste penetrates to a point 5 to 7 mm. from the bottom of the mould The apparatus is that used for the setting time test with the substitution of the plunger of 1 cm. diameter for the needle The percentage of water (P) to be used in gauging neat cement to a paste of normal consistency is defined as 0.78 times that obtained in the above test. Pastes of normal consistency are used for setting time and soundness tests. The percentage of water to be used in the strength tests on 1 . 3 cement sand mortars is determined by the formula $\frac{1}{4}P+2.50$.

Strength.—The strength is determined by a tensile test on briquettes, 1 sq in. cross section at the waist, made from a mortar composed of 1 part by weight of cement to 3 parts standard sand (18–25 British Standard mesh). After storing for 24 hours in moist air (58°–64°F, relative humidity not less than 90%) the briquettes are stored in water at 58–64°F. The mean tensile strength of six briquettes must not be less than 300 lb. per sq. in. at 3 days after gauging, and at 7 days after gauging it must show an increase on the value at 3 days and not be less than 375 lb. per sq. in. Strength tests on neat cement have now been abandoned except as an optional test, failure to pass which shall not involve rejection of the cement.

Setting Time—The setting time of normal setting cements shall not be less than 30 minutes for the initial set nor more than 10 hours for final set. For quick-setting cement the initial set shall not be less than 5 minutes nor the final set more than 30 minutes. The setting time is determined with a Vicat needle apparatus.

Soundness.—The soundness test is designed to ensure that the set cement shall not be subject to any expansion. In the form in which it is used this test detects the presence of dangerous amounts of free calcium oxide, the slow slaking of which may cause deferred expansion. The test is carried out by means of the Le Chatelier apparatus (Fig. 2), which consists of a small split cylinder of spring brass or other suitable metal 0.5 mm. thick forming a mould 30 mm. internal diameter and 30 mm. high. Two indicators, 165 mm. long, with pointed ends, are attached to either side of the split. The mould is placed on a small piece of glass and filled with neat cement paste of normal consistency and covered with another glass plate and submerged in water at 58°–64°F. for 24 hours. It is then boiled for 3 hours and the alteration in the distance apart of the indicator points measured. The expansion must not exceed 10 mm. or, in the event of its failing to comply with this test, 5 mm. subsequent to aeration for 7 days The limit allowed is so wide that cements rarely fail to pass the test.

OTHER SPECIFICATIONS.—The specifications in use in Europe and America follow the same general lines though the tests differ in some respects. Compression tests on mortar cubes are in most cases preferred to the tensile strength test, and pat tests are, in several instances, used for determining soundness.

RAPID HARDENING PORTLAND CEMENT—The demand for cement which would attain a higher strength at early ages than normal Portland cements has led to the production of rapid-hardening Portland cements. These cements have similar setting times to the normal product, but develop strength more

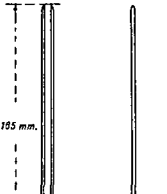


FIG. 2.

rapidly. The method of manufacture is similar to that of Portland cement, but the raw materials are often ground more finely to ensure greater uniformity in the clinker and the lime content often raised slightly. The clinker is ground more finely and the finished cement shows on an average about 1% residue on a 170 British Standard mesh sieve.

OTHER PORTLAND CEMENTS—White Portland cement is similar to normal Portland cement except in respect of colour. It is manufactured from raw materials low in iron oxide. Coloured cements are made by the addition of pigments to the white or normal grey cement. The pigments used are iron oxides and hydroxides, manganese dioxide, carbon blacks and chromium oxide. Waterproofed cements are Portland cements to which a small proportion of water-repellent substance such as calcium stearate has been added with the intention of decreasing the adsorption of concrete made from them. Natural Portland cement, the manufacture of which has now almost ceased, was made by

burning marls, or other naturally occurring mixtures of calcareous and argillaceous materials, of a composition approximating to Portland cement, without control of the composition or preparation of the raw materials. Roman cement belonged to this class.

Cements made from Blast-furnace Slag.

In the air-cooled condition blast-furnace slag has little or no hydraulic properties, but if suddenly chilled from the molten condition by running into water, or by other means, a product having cementitious properties may be obtained from suitable slags. The process of rapid chilling is known as "granulation," and the product as "granulated" slag. In general, slags of high lime content are granulated for use in cements, but some slags of high alumina content, as the Cleveland slag, also have similar properties.

Granulated slag only reacts with water relatively slowly and the addition of an activator is required to develop its latent cementitious properties. Lime, alkali sulphates, calcium and magnesium sulphates are activators. The theory of their action is not clearly understood. A mixture of hydrated lime and granulated slag, often with the addition of a small percentage of sulphate salts, forms what is known as a *cold process slag cement.* Though still produced in some European countries, manufacture in Great Britain has been abandoned in favour of Portland blast-furnace cement.

Portland blast-furnace cement is made by grinding together Portland cement clinker and granulated slag with a small amount of gypsum to control the set. In this cement, on hydration, the Portland cement portion liberates the calcium hydroxide required to activate the granulated slag. Both portions of the cement contribute to the hardening and development of strength. The British Standard Specification requires that the proportion of granulated slag in the cement shall not exceed 65%. In Germany two forms of blast-furnace cement are recognised, *Eisen-Portland* cement and *Hochofen* cement containing respectively 30% and 85% granulated slag as maxima. Typical analyses of a Scottish granulated slag used in Portland blast-furnace cement and of a Portland blast-furnace cement are as follows:

	Granulated Slag. %	Portland blast-furnace cement. %
CaO	47·0	57·1
SiO_2	33·0	23·5
Al_2O_3	14·0	8·6
FeO, Fe_2O_3	0·6	2·3
MnO	0·8	0·4
TiO_2	—	0·2
MgO	3·2	2·9
Na_2O	—	0·3
K_2O	—	0·6
SO_3	—	1·6
S (sulphide)	1·4	0·6
Loss on ignition	—	1·9

Portland blast-furnace cement is similar in physical properties to Portland cement and the British Standard Specification covering it is identical with that for Portland cement apart from the clauses relating to composition and mode of manufacture. In composition Portland blast-furnace cement is required to conform to the following maximum limits:

Ignition loss 3%, magnesia 5%, sulphur present as, and calculated as, sulphur trioxide 2%, sulphur present as sulphide and calculated as sulphur 1·2%.

Apart from its use in Portland blast-furnace cement granulated slag is also sometimes used as a raw material for Portland cement manufacture, replacing the clay and part of the limestone. The product obtained on burning is a Portland cement differing in no way from that obtained from the usual raw materials.

Pozzolanas and Pozzolanic Cements.

Certain natural materials of volcanic origin and some artificial products have the property of combining with lime in the presence of water at ordinary temperatures to form cementitious compounds. Such materials are classed as natural or artificial pozzolanas. The natural pozzolanas are volcanic ash materials existing as incoherent tuffs or as semi-compacted or compacted rocks. The ash has in some cases suffered considerable chemical alteration subsequent to deposition owing to the action of superheated steam and carbon dioxide below the earth's surface. The properties of pozzolanas were known to the Greeks and Romans and it is from the name of the place where one such material was obtained, Pozzuoli, near Naples, that the term pozzolana is derived. Natural pozzolanas at present widely used in Europe are the various Italian pozzolanas, Rhenish Trass, and Santorin Earth from the Grecian isle of Santorin. Other pozzolanas are Tosca obtained from Teneriffe, and Tetin from the Azores. The principal artificial pozzolanas are those produced by the burning of clays and shales at temperatures varying from 600° to 950°C. The burning temperature for optimum activity is rather critical. Crude burnt clay pozzolanas produced by burning clay in heaps have long been used in India and Egypt under the names *Surkhi* and *Homra*, while ground lightly burnt clay tiles were used for this purpose by the Romans. The composition of some pozzolanas is as follows:

	Rhenish Trass. %	Italian Pozzolanas		Burnt Clay Pozzolana. %
		Rome. %	Naples. %	
Loss on ignition	10·1	6·2	7·2	1·3
SiO_2	55·2	46·5	56·7	60·2
Al_2O_3	16·4	18·7	16·9	17·7
Fe_2O_3	4·6	10·9	6·3	7·6
TiO_2	0·6	—	—	1·2
CaO	2·6	9·6	3·6	2·7
MgO	1·3	3·0	0·5	2·5
K_2O	4·3	2·0	4·1	3·2
Na_2O	5·0	2·3	2·9	1·0
SO_3	0·2	—	—	2·5

Pozzolanas are used in mixtures both with lime and Portland, or Portland blast-furnace, cement. In lime mortars they confer on non-hydraulic limes the property of setting under water. Such mixtures have been much used in Southern Europe for constructional work in sea-water, and also in Northern Europe as a general building mortar.

The setting of Portland cement results in the liberation of a considerable amount of calcium hydroxide which is capable of combining with a pozzolana. The addition of pozzolanas to Portland cement therefore increases the total amount of cementitious constituents produced and renders the set product more resistant to attack by sea water or certain other chemically destructive agencies. The use of trass for concretes in sea-water, and generally in inland water, has been common practice for many years in Germany and other European countries Formerly it was customary to add the trass, ground to about 30% residue on a 170 British Standard mesh sieve, as a separate ingredient, along with the cement and aggregate to the concrete mixer It is now, however, preferred to premix the trass and cement and to grind the trass more nearly to cement fineness. The proportions of trass to cement recommended are:

High lime Portland cement—0 66 cement. 0 34 trass

Low lime Portland cement—0 75 cement · 0 25 trass.

Portland blast furnace cement—0 80 cement 0 20 trass.

Premixed and bagged pozzolanic cements *containing Portland cement and a pozzolana are* now marketed in various countries The pozzolana used in Great Britain is burnt clay, in Germany trass, in France gaize (a heat-treated highly siliceous rock containing a proportion of clay), and in Italy the volcanic ash deposits which are sometimes heat treated to increase their activity.

Aluminous Cement.

Aluminous cement was first marketed commercially in 1918. It was developed as the result of the investigations of Bied in France into the production of cements more resistant than Portland cement to attack by natural waters containing high contents of sulphate salts. It is characterised not only by a very high degree of resistance to chemical attack, but also by very rapid hardening properties. The cost is about twice that of Portland cement. Aluminous cement is manufactured by fusing (occasionally by sintering) a mixture of bauxite and limestone in a reverberatory open hearth furnace, in an electric furnace, or occasionally in a rotary kiln. The bauxite must be fairly low in silica (*e g.* 5%) but a considerable content of ferric oxide is not objectionable. The reverberatory furnace, about 8 ft. wide and 12 ft. long excluding *the stack, is fired with pulverised coal, the raw* materials being continuously charged in through the stack. Fusion takes place on the hearth at a temperature around 1,550°–1,600 C. and the molten product pours out continuously into moulds. Furnaces of the dimensions mentioned produce about 30 tons of cement per day. The rate of cooling needs to be suitably adjusted as it affects the rate of setting and hardening The cement is crushed and passed through magnetic separators to remove metallic iron and then ground in tube mills to a fineness of about 10% on a 170 mesh. No additions are made during grinding. Electric furnaces are of the arc type and are only economical where electric power is very cheap. The rotary kiln is used only in the United States of America.

The composition of aluminous cements varies more widely than that of Portland cement. Some typical analyses are as follows:

	%	%	%	%
SiO_2	5·1	3·7	5 4	7 0
Al_2O_3	38·9	41 9	36 0	36 5
Fe_2O_3	11·0	12 0	5 6	4 0
FeO	5·8	1·7	10 5	9 5
TiO_2	1·7	1·7	2 2	2 0
CaO	36 6	36 4	38 8	40 3
MgO	0 2	1·4	0 3	—
Na_2O	0·1	—	—	—
K_2O	0 3	—	—	—
SO_3	0 2	1·2	0 0	—
	99 9	100 0	99 8	99 3

In general the silica is kept as low as the raw materials permit and it is preferred that the iron should be in the ferric rather than the ferrous condition. The principal compounds present in aluminous cement are one or more of the calcium aluminates $CaO\ Al_2O_3$, $3CaO{\cdot}5Al_2O_3$, $5CaO\ 3Al_2O_3$. The silica is present as $2CaO{\cdot}SiO_2$ or $2CaO\ Al_2O_3\ SiO_2$ (gehlenite). Ferric iron is probably present as a solid solution, while ferrous iron may possibly be present in magnetite. Both the compounds $CaO\ Al_2O_3$ and $3CaO\ 5Al_2O_3$ have excellent rapid hardening properties, but $5CaO\ 3Al_2O_3$ is inferior in this respect. Di-calcium silicate (*see earlier) is slow hardening, but gehlenite* ($2CaO\ Al_2O_3\ SiO_2$) has no hydraulic properties.

On hydration in excess water the calcium aluminates in aluminous cement form alumina gel and crystalline hydrated dicalcium aluminate ($2CaO\ Al_2O_3{,}8H_2O$), but there is some evidence that when gauged with limited amounts of water as in actual use a hydrated mono-calcium aluminate gel may be formed initially.

Physical and Mechanical Properties.

The setting time of aluminous cement is similar to that of Portland cement and is determined in the same manner. Soundness is commonly tested by the Le Chatelier apparatus The tensile strength of aluminous cement, as ascertained by tests on mortars similar to those used in the British Standard specification for Portland cement, is somewhat misleading when comparison is made with *Portland cement* The low water content (about 8% by weight of the mortar) specified in this form of test is insufficient to hydrate the aluminous cement fully and the strength obtained bears a lower relation to that obtained in concrete than is the case for Portland cement as indicated by the following data.

	Compressive strength lb. per sq. in. 1:2:4 concrete at 1 day.	Tensile strength lb. per sq. in. 1:3 B.S. mortar briquettes at 1 day.
Aluminous Cement	7,370	540
Rapid Hardening Portland Cement	740	350

Tests on plastic mortars of higher water content give more comparable data. Aluminous cement develops strength very rapidly and approaches its maximum strength within one day, compared with seven days and upward for Portland cement. The heat evolution is correspondingly rapid and averages about 75 calories per gram of cement at one day. The strength of aluminous cement is seriously decreased by high temperatures and it is necessary to place aluminous cement concrete in small vertical lifts at intervals of say, a day, in order to avoid overheating of the concrete.

Aluminous cement at normal temperatures has a very high resistance to attack by sulphate-bearing water, sea-water, and also by slightly acid waters such as obtain in moorland areas.

Uses of Cement.

Cements are used both in the form of mortar and of concrete. Mortars, which are mixtures of cement with sand, are used mainly as a bonding material in brickwork or masonry, or as a surface covering as in renderings and stucco. Plain cement mortar is more suitable for bedding engineering bricks than building bricks. For the latter, mortars made from hydraulic lime or high calcium lime mixed with a proportion of cement are to be preferred. In concrete the cement is used to bond together an aggregate consisting of sand and gravel, or other hard materials, into a solid mass. This forms by far the largest application of cement. Concrete is used for building work of all types, for massive engineering structures, for roads, and for numerous other purposes. F. M. L.

In addition to its application in concrete used *in situ* large quantities of cement are used in the manufacture of concrete products made in suitably equipped factories and transported to the building site.

Concrete Tiles are now made in large quantities and compete very closely with clay tiles in some districts. The tiles are made from a mixture of about one part of cement to three parts of graded sand which should be of good quality. A proportion of calcium chloride—about 2% of the weight of the cement—is often added in cold weather to accelerate the rate of setting and hardening. British Standard Specifications exist for plain (No. 473) and interlocking concrete tiles (No. 550) as well as for plain clay tiles (No. 402). Tiles of either material conforming with these specifications may be purchased with assurance of satisfactory service.

As a result of the demand for colour in concrete tiles, large quantities of pigments are consumed by the industry. Suitable pigments must be of high staining power, fast to light and lime, and not contain more than 2·5% of soluble sulphates. These requirements are met by the mineral oxides and hydroxides, $Fe(OH)_3$, Fe_2O_3, MnO_2, Fe_3O_4, by chromium oxide and by carbon.

Concrete Flags, Kerbs, and Pipes are also largely used. Standards for their properties and limitations of the characteristics of the materials to be used are given in the appropriate British Standard Specifications Nos. 368, 340, and 556 respectively.

Precast Concrete Lightweight Partition Blocks (British Standard Specifications Nos. 492 and 728) are an important building material. F. L. B.

Concrete has the property of high compressive strength, but a relatively low tensile strength. This deficiency of concrete is remedied in reinforced concrete in which mild steel rods, bonded together by steel hooks and wire, are employed. The reinforcement is placed in such a position as to take the tensile stresses to which the reinforced concrete will be subject and the concrete poured round it. On hardening, the cement adheres strongly to the steel reinforcement and the composite material is able to withstand both high tensile and compressive stresses. The principles of design of reinforced concrete are set out in " Report of the Reinforced Concrete Structures Committee of the Building Research Board " (H.M. Stationery Office). This report describes the characteristics of good concrete aggregates and sets limits for certain impurities. The proportioning of aggregate and cement for concrete of various qualities is also dealt with and standard methods for testing the strength of concrete are described.

The temperature coefficients of expansion of mild steel and concrete are very similar, this fact having an important bearing on the stability of reinforced concrete. The concrete covering the steel protects it from corrosion and this protection is enhanced by the alkaline medium formed in set cements by the hydration reactions. If, however, the concrete covering is too thin, or becomes seriously cracked, corrosion of the reinforcement can occur, and the expansion accompanying this disrupts the concrete. Impermeable concretes are required for reinforced concrete work and an adequate cover is particularly necessary when the material is to be exposed to sea-water or other natural or artificial destructive agencies.

Although concrete made from Portland or other types of cements is on the whole a permanent material, there are certain conditions under which serious deterioration and ultimate failure may occur. These are conditions where the concrete is exposed to chemical agents, aqueous or gaseous, which react with the cement. The hydration products of Portland cement are all decomposed by water and when, therefore, water is able to pass continuously through a concrete the lime is progressively leached from the set cement compounds leaving eventually an incoherent mass. In practice good concrete has a very low permeability and no appreciable percolation occurs, unless the water

pressure is very high, and with most waters any action is limited to a very thin surface skin.

With hard waters a concrete which is initially slightly permeable often tends to seal up. Waters which are very pure, or slightly acid due to the presence of free (aggressive) carbon dioxide, have a more serious action. On even dense concretes the surface cement may become dissolved away to an appreciable depth and the aggregate left exposed. Aluminous cement is much more resistant and no appreciable surface action occurs. Natural groundwaters in some areas contain sulphate salts which have a destructive action on Portland cement concrete. Thus gypsum (calcium sulphate) and magnesium sulphate are found in Great Britain in some clays and soils while alkali sulphates occur in some countries abroad The latter sulphate salts react with the free calcium hydroxide in set Portland cement to form calcium sulphate, and with the hydrated calcium aluminate to form calcium sulphoaluminate. The formation of the latter compound is accompanied by a considerable expansion causing disruption of the concrete. Ammonium sulphate is particularly destructive in its action on Portland cement concrete. Pozzolanic cements and Portland blast furnace cement are more resistant to sulphate attack than Portland cement, while aluminous cement concrete properly made is completely resistant.

Sea-water, owing to its content of sulphate salts, acts chemically on Portland cement concrete, and concrete must be made very dense and impermeable to resist its action. The other cements previously mentioned are again more resistant than Portland cement to chemical attack by sea water.

Concrete is also attacked chemically by various agents encountered in industry. Vegetable oils and fats, sugar solutions, particularly when hot, and various inorganic salts act in this way. With many of these substances, a greater resistance to attack may be obtained by the use of pozzolanic cements and aluminous cement instead of Portland cement. Some gases also attack concrete in the presence of moisture. Thus sulphur dioxide has sometimes been a source of trouble in chimneys when the temperature of the exit gases is sufficiently low for condensation to occur. In sewers the evolution of hydrogen sulphide from sewage, followed by its oxidation to sulphuric acid, may cause attack on mortar or concrete. There are many surface treatments, *e g.* with bitumen solutions, silicates, fluosilicate, that are applied to concrete to render it more resistant to chemical attack. The efficiency of these treatments varies very widely with their nature and the conditions to which they are exposed.

Lightweight Concretes.

Lightweight concretes represent a special form of concrete in which strength has been sacrificed in varying degree to obtain lightness Dense concretes made with the usual heavy aggregates weigh about 140–150 lb. per cu. ft, the corresponding figures for lightweight concretes being 40–100 lb. per cu. ft. One form of lightweight concrete which has been used to a limited extent for the manufacture of precast units is made from sand or other fine aggregate, and cement with the addition of a small proportion of aluminium powder. Evolution of hydrogen occurs as a result of reaction between the aluminium powder and the calcium hydroxide liberated in the setting of the cement The mass swells and sets in an expanded condition with a honeycomb structure. Other methods to obtain a similar end have also been employed

The main form of lightweight concrete is that in which aggregates of light weight such as pumice, foamed and granulated slag, expanded clay, coke breeze, and clinker are used. Additional reduction in weight is also obtained in cases where porosity is unimportant by omitting, or much reducing, the proportion of material of sand fineness. Clinker and coke breeze may, unless carefully selected, result in expansion and unsoundness of concrete made from them. The other lightweight aggregates are satisfactory in this respect. The shrinkage of lightweight concretes on drying is not infrequently a source of many minor troubles in building. It varies much, however, with the different aggregates, and the best materials give concrete with shrinkage little, if any, above that of normal heavy concretes.

Lightweight concretes are used for screedings on floors and roofs, for precast partition slabs, fixing and walling blocks, and also to some extent in filler joist floors and reinforced concrete floor slabs. Coke breeze and clinker are unsuitable for use in those cases in which the concrete is in contact with steel either as reinforcing bars, floor joints, or structural steelwork, owing to the serious risk of corrosion. The strength of lightweight concretes can be increased by suitable grading of the aggregate or the addition of sand as fine aggregate The weight is increased at the same time. Light weight concretes have much better heat insulating properties than normal concretes but a lower resistance to transmission of sound. The presence of many air filled cavities is responsible for the former, but it acts in the converse sense in respect of acoustic properties, since sound insulation increases with mass per unit surface area of the building unit.

Bibliography —F. M. Lea and C. H. Desch, "Chemistry of Cement and Concrete," Arnold, 1935; E. C. Eckel, "Cements, Limes, and Plasters," John Wiley, 1928; for manufacturing details, *see* A. C. Davis, "Portland Cement," Concrete Publications, 1934; Building Research Bulletin No. 15, "Lightweight Concrete Aggregates"; No. 5, "The Properties of Breeze and Clinker Aggregates and Methods of Testing their Soundness"; Building Research Special Report No. 15, "The Corrosion of Steel by Breeze and Clinker Concretes."

F. M. L.

VII. Sand-Lime Bricks.

Sand lime bricks may be included among the more modern building materials. They are manufactured by moulding a moist mixture of sand and lime into the form of bricks, and hardening by exposure in autoclaves to high-pressure steam.

The process was originally devised and patented in England by Van Derburgh (B.P. 2470, 1866) and developed and patented in Germany by W. Michaelis (G.P. 14195, Kl. 80, 1880). Only patents concerning details of machinery are now valid.

Although commercial production began less than fifty years ago in Germany, these bricks are now widely used in many countries. The output in recent years has fluctuated with world economic conditions, but was stated to be about 1,000,000,000 in Germany in 1928, and 320,000,000 in the U.S.A. in 1927. In Great Britain, where, owing to the relative abundance of clays suitable for brick-making, the need for alternative materials has not been so great, it is believed to be about 100 to 150 million at the present time (1935).

The cost of production is such that when manufactured in a favourable locality the average quality sand-lime brick can generally be sold at prices competing with those of common clay brick. The better grades for facing work, or where unusually high strength is required, sell at prices above those of common clay brick but at much lower prices than good clay facing bricks.

Manufacture.

(a) *Raw Materials.*—The materials required are sand and either lump lime (quicklime) or hydrated lime (dry hydrate), according to the process used.

The sand must be available at or near the site of the works, since it constitutes 90% or more of the brick; the lime may be brought from a distance. The requirements of the sand are that it shall not contain an excessive amount of clay (i.e. not over 3–4%). Soluble salts, organic matter, or any mineral matter coating the sand grains are also objectionable. The size grading of the sand grains has important effects upon the quality and texture of the bricks.

The lime used is generally of the high-calcium type (either white chalk lime or mountain lime), but other types of lime can be used provided that the all-important criterion of "soundness" be satisfied. This requires that the lime shall be completely hydrated before use, if dry hydrate be used, or shall hydrate readily and completely during the drum- or silo-hydration processes when quicklime is used. If this condition is not fulfilled, further hydration occurs during the autoclaving process with resulting expansion, and the bricks are weakened and frequently burst. Such hydration and expansion is always completed in the autoclave and will not occur in bricks after use. Lime may readily be tested for any such unsoundness or liability to further hydration and expansion.

The proportion of lime used is normally from 5–8% (calculated as calcium oxide) of the weight of the brick. The water content of the mix before pressing is just sufficient for the mass to cohere if pressed together in the hand; an excess of water must be avoided.

(b) *Process.*—The process of manufacture involves three stages: mixing, pressing, and hardening. The three principal variations in the process occur in the first stage.

In (i) *The Dry Hydrate Process* dry hydrated lime is mixed with the sand and necessary water and the mix fed directly to the presses.

In (ii) *The Silo Process* ground quicklime is mixed with the sand and a proportion of water slightly above that required for hydration, and the mix stored for about 24 hours in a silo, where complete hydration of the lime takes place. The material is then remixed with the water necessary for the correct consistence for pressing.

In (iii) *The Drum Hydration Process,* also using quicklime, hydration is achieved by mixing the quicklime, sand, and water in a large rotating drum for 20 to 30 minutes. A steam pressure of up to 60 lb. per sq. in. supplied partly by the heat generated by the hydration of the lime and partly by steam injection is maintained during the latter part of this period to accelerate the hydration. The mix is then discharged to a secondary mixer where any further water necessary is incorporated, and thence to the presses.

Rotary table presses, which may have an output of up to 3,000 bricks per hour, are generally used for moulding the bricks. Very high moulding pressures are necessary and the presses have therefore to be very robust and the mould liners extremely hard. The pressures used vary considerably, and are adjusted to give a brick which can be handled from the press without damage. In experimental work bricks of maximum strength have been obtained with pressures of about 6 tons per sq. in. on the brick; the pressures used in practice are probably well below this.

Hardening is carried out in autoclaves 30 ft. to 70 ft. in length and 5 ft. 6 in. to 7 ft. in diameter. The bricks are loaded on to trucks directly from the presses, and the trucks run into the hardening chambers on rails. The duration of treatment and steam pressures used vary from 8 to 12 hours at 120 lb. per sq. in. to 4 to 6 hours at 200 lb. per sq. in. In general the longer times and higher pressures give bricks of better quality.

The bricks may be used within a few hours of leaving the autoclaves.

Properties.

The characteristic properties of these bricks are accurate size and shape, white colour, and consequently good light-reflecting properties, and lack of any tendency to efflorescence. The compressive strength varies in bricks of different qualities from about 1,000 to 5,000 lb. per sq. in. and the transverse strength (modulus of rupture) from about 200 to 750 lb. per sq. in. (in both cases when tested in the wet state). The ratio of wet to dry strength varies but has an average value of about 0·65. On account of the possibility of a very low ratio, testing in the wet state is preferable.

The durability of sand-lime bricks of good quality is satisfactory. Poor quality sand-lime bricks, badly made, or made from indifferent materials, are, however, unsuitable for exposed external work.

The drying shrinkage and moisture movements vary but are usually higher than with clay brick and of a similar order to those of cement

concrete. The resistance to fires of moderate intensity appears to be satisfactory, judging from laboratory tests which have been made, but in more intense fires some tests have shown good clay bricks to have some superiority (R. Schlyter, Statens Provningsanstalt, Meddelande 50, Stockholm, 1931).

In other properties, including adhesion of mortar and plaster, thermal conductivity, and resistance to rain penetration, there is no outstanding difference from clay brick.

Chemical Constitution.

The hardening of sand-lime bricks in the autoclave is due to the reaction of lime with sand with formation of a hydrated calcium silicate. The silicate formed is usually colloidal in nature and has not been definitely isolated nor is its composition known with any certainty (G. Grime and G. E. Bessey, Trans. Ceram. Soc. 1933, 32, 14–20)

Free lime (calcium hydroxide) should not be present in appreciable quantities in a well made brick; it has no cementitious value and is probably deleterious

Atmospheric carbon dioxide slowly decomposes the silicate with formation of calcium carbonate and hydrated silica. This is in no way harmful to the brick and it is, indeed, found that the bricks increase in strength with exposure through the occurrence of this reaction

Use.

Sand lime bricks are used in building in the same way as clay bricks. It should, of course, *be remembered that bricks from different makers* may vary in the same way as different clay bricks, and hence treatment in plastering, for example, may have to be modified slightly to suit any particular brand of brick.

Choice of these bricks should be guided by the British Standard Specification (No 187, 1934) and by the appearance where they are to be used for facing. The specification describes three classes of bricks:

I. Bricks for special purposes.
II. Building Bricks, class A.
III. Building Bricks, class B

The first class should be used where very high strength is required, or where the bricks are to be used in very exposed positions (parapets, sills, below damp course, etc.); class A building bricks are suitable for all general facing work and class B building bricks for internal work only.

The tests included in the specification are for strength and chemical composition. A minimum silica content ensures that the bricks are made from silica and lime, whilst a maximum limit for free lime and a minimum limit for calcium oxide present as silicate ensure that the bricks have been properly manufactured.

Bibliography.—G. E. Bessey, Building Research Special Report No. 21, H.M. Stationery Office, London, 1934, pp. 1–62; W. E. Emley, U.S. Bureau of Standards Technical Paper No. 85, Washington, 1917, pp. 1–41; A. B. Searle, "Bricks and Artificial Stones of Non plastic Materials," London, 1915, pp. 1–149; E. Leduc and C. de la Roche, Conservatoire des Arts et Métiers, Bull. No. 13, Paris, 1908, pp. 1–122.

G. E. B

BULBOCAPNINE. An alkaloid from tubers of *Dicentra canadensis* and *Corydalis cava*. Bulbocapnine hydrochloride, a white crystalline powder, soluble in water. Antispasmodic.

BULTFONTEINITE, $2Ca(OH,F)\cdot SiO_2$. It occurs as pink spherules of radiating triclinic needles as a secondary mineral in the Bultfontein diamond mine at Kimberley, South Africa. A portion of the lime is extracted by water and, after ignition, a further smaller portion is extracted; the formula is therefore written as $2Ca(OH)_2\cdot 2SiO_2\cdot Ca(OH)_2\cdot CaF_2$ (*cf.* afwillite) (J. Parry, A. F. Williams, and F. E. Wright, Min. Mag. 1932, 23, 145).

L. J. S.

BUNTKUPFERERZ *v.* BORNITE.

BUPLEUROL,

$$Me_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(:CH_2)\cdot CH_2\cdot CH_2OH\ ?$$

Francesconi and Sernagiotto (Atti R. Accad. Lincei, 1913 (v), 22, I, 34, 148) separated from the essential oil obtained from the leaves and flowers of *Bupleurum fructiosum*, L., a primary alcohol, *bupleurol*, $C_{10}H_{20}O$, b.p. 209°–210°/762 mm., $d^{17°}$ 0.8490, n_D 1.4503, $[\alpha]_D$ ±0°, *phenylurethane*, m.p. 45°. On oxidation with chromic acid it gives an aldehyde, *bupleural*, *semicarbazone*, m.p. 135°. The constitution of the alcohol has not been determined; Francesconi and Sernagiotto suggest the representation given above on the grounds that the other main constituent of the oil is β phellandrene.

J. L. S.

BURKHEISER'S PROCESS *v.* AMMONIA.

BURMITE *v.* AMBER or SUCCINITE.

BURRSTONE or BUHRSTONE. A hard, tough rock consisting of chalcedonic silica with a cellular texture, especially suitable for use as millstones for grinding corn, paints, etc. It is white, grey or creamy in colour. The best stones are from the Tertiary strata of the Paris basin, and have originated by the silicification of fresh-water limestones, the cellular spaces representing the casts of fossil shells and *Chara* seeds.

L. J. S.

BUSH SALT. A light-brown or greyish powder prepared by the natives of Ssonges by lixiviating the ashes of the sedge, *Cyperus Haspan*, L. Contains 77.77% KCl, and 18.48 K_2SO_4, with traces of sodium salts and organic matter (Lenz, Ber. deuts. Pharm. Ges. 1911, 21, 270).

BUSZITE. Silicate of the rare-earths Nd, Pr, Er, and Eu. A single small ditrigonal bipyramidal crystal with yellowish red colour and resinous lustre has been found with beryl at Khan in South-West Africa (E. Steinwachs, Centr. Min. A, 1929, 202).

L. J. S.

BUTADIENE. This hydrocarbon exists to the extent of about 10% in the fraction of vapour-phase cracked gases that contains butane and the butenes. It is not at the moment feasible to separate butadiene from this mixture, because under mild conditions of polymerisation over a phosphoric acid catalyst the C_4 un-

saturated hydrocarbons produce liquid hydrocarbons within the boiling range of motor spirit. Further, it is possible by simple thermal treatment to obtain higher polymers serviceable for motor spirit and of a high octane value. Other synthetic products from this hydrocarbon are discussed under the heading of *Cracking, see* PETROLEUM. A. E. D.

BUTADIENES AND POLYOLEFINS (Conjugated). These substances are hydrocarbons which possess two or more double linkages in the molecule, the double linkages being conjugated, *i.e.* occupying alternate positions with single linkages. The most important members of the group are butadiene, hexatriene, and their alkyl- and aryl- derivatives, but the group includes among its higher polyene members the important carotenoid hydrocarbons, α-, β-, and γ-carotene, and lycopene (*q.v.*).

The butadienes and hexatrienes contain the carbon skeletons C:C·C:C and C:C·C:C·C:C respectively, and they are formed by very numerous elimination reactions in which the elements of water, hydrogen halide, alkylamines (or their salts), etc., are removed from suitable glycols, unsaturated alcohols, dihalogenoparaffins, halogeno-olefins, or alkenyl ammonium hydroxides. These eliminations sometimes proceed spontaneously, but usually they are brought about by the action of heat, catalysts, bases, etc. In many reactions migration of a double linkage takes place to yield a conjugated compound where otherwise a non-conjugated compound would be expected. A great variety of glycols and unsaturated alcohols suitable for the syntheses of alkyl- and aryl-butadienes can be obtained by the Grignard reaction. Typical of the elimination reactions are the following, the catalysts (where employed) being shown in brackets:

(1) $CMe_2(OH)\cdot CH{:}CH_2 \xrightarrow{\text{Heat (HBr)}} CH_2{:}CMe\cdot CH{:}CH_2 + H_2O$
Isoprene.

(2) $CHMe{:}CH\cdot CHMeOH \xrightarrow{\text{Heat (Kaolin)}} CHMe{:}CH\cdot CH{:}CH_2 + H_2O$
Piperylene.

(3) $CMe_2(OH)\cdot CH_2\cdot CHMeOH \xrightarrow{\text{Heat (HBr)}} CH_2{:}CMe\cdot CH{:}CHMe + H_2O$
αγ-Dimethylbutadiene.

(4) $CMe_2Br\cdot CMe_2Br + 2NaOH \longrightarrow CH_2{:}CMe\cdot CMe{:}CH_2 + 2NaBr$
βγ-Dimethylbutadiene.

(5) $CH_2Br\cdot CH{:}CH\cdot CH_2Br + Zn \longrightarrow CH_2{:}CH\cdot CH{:}CH_2 + ZnBr_2$
Butadiene.

(6) $NMe_3(OH)\cdot[CH_2]_4\cdot NMe_3OH \xrightarrow{\text{Heat}} CH_2{:}CH\cdot CH{:}CH_2 + 2H_2O + 2NMe_3$
Butadiene.

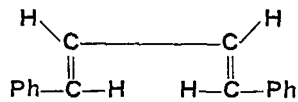
(7) $CHMe{:}CMe\cdot CHMeCl + C_9H_7N \longrightarrow CHMe{:}CMe\cdot CH{:}CH_2 + C_9H_7N,HCl$
αβ-Dimethylbutadiene.

In certain cases, especially where groups such as $>CH\cdot CH(OH)\cdot CH<$ occur, elimination can take more than one course, corresponding to the different possible ways of splitting off the eliminated molecule. In such circumstances mixtures of hydrocarbons are produced; thus, in reaction (3) above, a little of the diene

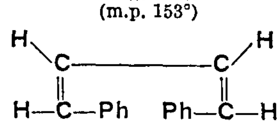
$$CMe_2{:}CH\cdot CH{:}CH_2$$

is formed in addition to the main product, and in the dehydration of $CH_2{:}CH\cdot CH_2\cdot CMe_2\cdot OH$ one unconjugated and two conjugated dienes, *viz.* $CH_2{:}CH\cdot CH_2\cdot CMe{:}CH_2$, $CH_2{:}CH\cdot CH{:}CMe_2$ and $CHMe{:}CH\cdot CMe{:}CH_2$, are formed side by side (Bacon and Farmer, J.C.S. 1937, 1065).

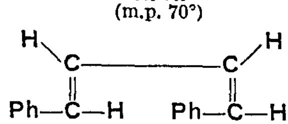
Physical Properties.—All the earlier members of the group, save butadiene, which is gaseous, are liquids of low specific gravity and low dielectric constant. The diene and triene members are colourless, but the higher polyene members are coloured and may be solid. Many compounds of the group are theoretically capable of showing geometrical isomerism, and it is probable that the considerable ranges of boiling-point recorded for various of the alkylbutadienes are due in part to the occurrence of *cis-trans* isomerism (*see* Farmer and Warren, J.C.S. 1931, 3221); in the example of αδ-diphenylbutadiene three geometrical isomerides have been isolated (Straus, Annalen, 1905, **342**, 214).



trans-trans
(m.p. 153°)



cis-cis
(m.p. 70°)



cis-trans
(oil).

Chemical Properties.—The members of the butadiene group possess very strong additive tendencies, uniting with 1 mol. of certain reagents and either 1 or 2 mols. of others. With 1 mol. of bromine or chlorine (X) they yield dihalides of one or more of the types:

$$\underset{1}{>CX}\cdot\underset{2}{\dot{C}X}\cdot\underset{3}{\dot{C}}{:}\underset{4}{C<} \quad \text{(1:2-addition)}$$

$$\underset{1}{>C}{:}\underset{2}{\dot{C}}\cdot\underset{3}{\dot{C}X}\cdot\underset{4}{CX<} \quad \text{(3:4-addition)}$$

$$\underset{1}{>CX}\cdot\underset{2}{\dot{C}}{:}\underset{3}{\dot{C}}\cdot\underset{4}{CX<} \quad \text{(1:4-addition)}$$

and with 2 mols., tetrahalides,

$$>CX\cdot\dot{C}X\cdot\dot{C}X\cdot CX<.$$

With 1 mol. of hydrogen halide they yield hydrohalides of one or more of the types:

$$\underset{1}{>CH}\cdot\underset{2}{\dot{C}X}\cdot\underset{3}{\dot{C}}{:}\underset{4}{C<} \quad \text{(1:2-addition)}$$

$>\mathrm{C\,\dot{C}\,\dot{C}X{\cdot}CH}<$ (3 4 addition)
$\quad$ 1 2 3 4

$>\mathrm{CH\,\dot{C}.\dot{C}\,CX}<$ (1:4 addition)
$\quad$ 1 2 3 4

$>\mathrm{CX{\cdot}\dot{C}.\dot{C}{\cdot}CH}<$ (1.4-addition),
$\quad$ 1 2 3 4

and with 2 mols, di-hydrohalides of (as yet) undetermined orientation. With 1 mol. of hypochlorous acid they yield chlorohydrins of one or both of the types

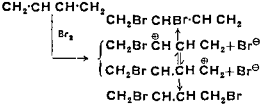
$>\mathrm{CCl\,C(OH)\,\dot{C}{\cdot}C}<$
$\quad$ 1 2 3 4

$>\mathrm{C\,\dot{C}\,\dot{C}(OH){\cdot}CCl}<,$
$\quad$ 1 2 3 4

and with 2 mols, di chlorohydrins The 1 4-(terminal) and 1.2- forms of the mono-addition products often occur side by side, owing probably to the tautomeric capacity of an intermediate additive form common to both, which readily undergoes the αγ-change

$(>\mathrm{CX{-}C{=}C}<\longrightarrow>\mathrm{C{=}C{\cdot}CX}<)$

and thus is able to lead to either or both of two final products when addition is complete:



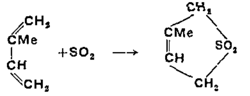
The same kind of isomerism has been observed amongst the addition products of hexatriene, and doubtless applies also to the conjugated polyenes.

When hydrogenated catalytically the butadienes yield olefins or paraffins, the orientation of the addendum at the dihydro stage depending on the nature and position of the substituent groups in the carbon chain The following approximate compositions of reaction mixtures have been observed by Lebedev and Yakubchik (J.C.S. 1928, 832, 2192) at the stage of 50% hydrogenation (platinum catalyst):

50% HYDROGENATION.

Diene.	Composition of Product
Butadiene . . .	Butane (34%), Δ^{α}-butene (23%), Δ^{β}-butene (9%), butadiene (34%).
α-Methylbutadiene (Piperylene)	Pentane (32%), propylethylene (10%), *s*-methylethylethylene (26%), piperylene (32%).
β-Methylbutadiene (Isoprene)	*iso*Pentane (30%), *iso*-propylethylene (12%), *as*-methylethylethylene (13%), trimethylethylene (15%), isoprene (30%).
βγ-Dimethylbutadiene	βγ-Dimethylbutane (28%), *as*-methylisopropylethylene (27 4%), tetramethylethylene (16 6%), βγ-dimethylbutadiene (28%).

The butadienes also unite with ozone to yield mono- or di ozonides, and often unite spontaneously with oxygen to yield peroxide derivatives. With sulphur dioxide they yield monomeric or polymeric cyclic sulphones,



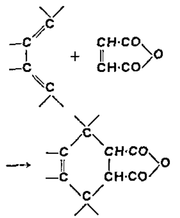
Isoprene. Isoprene sulphone
(2 methyl Δ^2-butene-1 4 sulphone)

and with selenium dioxide cyclic selenones analogous in constitution to the sulphones.

MELTING POINTS OF SULPHONES AND SELENONES.

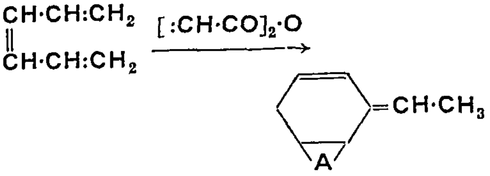
Butadiene.	Sulphone	Selenone
β-Methyl-	63°	67°
βγ-Dimethyl- . . .	135°	66°
β Phenyl-	133°	90°
βγ Diethyl- . . .	—	132°
βγ Diphenyl . .	183°	89°

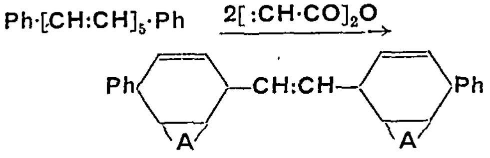
When warmed with maleic anhydride the butadienes yield crystalline anhydro*cyclohexenes, often in quantitative yield, the reagent* attaching itself to the terminal carbon atoms of the butadiene system (Diels-Alder reaction; *see* Annalen, 1928, 460, 98; 1929, 470, 62; Ber. 1929, 62, [B], 2081):



The hexatrienes and higher polyenes react similarly with maleic anhydride, the reagent *attaching itself to the terminal carbon atoms* of one or other of the butadiene systems (Farmer

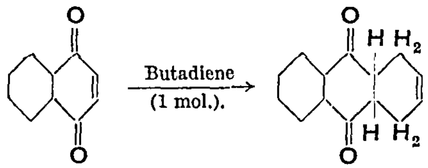
and Warren, J.C.S. 1929, 897; Kuhn and Wagner-Jauregg, Ber. 1930, 63, [B], 2662).



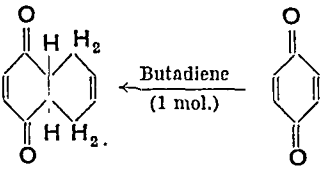


(A = ·CO·O·CO·)

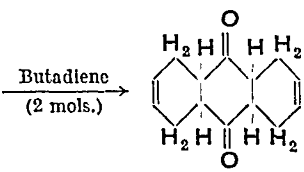
All these derivatives have reasonably sharp melting-points and serve to characterise the hydrocarbons. Analogous *cyclo*hexene derivatives are formed with acraldehyde, acrylic ester, and other systems containing the group ·CH:CH·CO, those with naphthaquinone and quinone



Naphthaquinone. Tetrahydroanthraquinone.



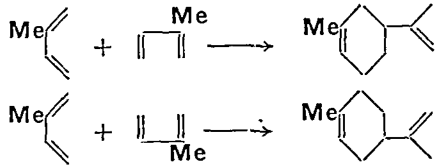
Tetrahydronaphthaquinone. Quinone.



Octahydroanthraquinone.

being particularly interesting and valuable owing to their hydroaromatic nature and consequent capacity to yield aromatic compounds by simple means. The Diels-Alder reaction thus affords a direct means of synthesis for numerous naphthalene and anthracene derivatives; moreover, the naphthaquinone addition products, like the maleic anhydride derivatives, are suitable for the characterisation of the conjugated dienes and polyenes.

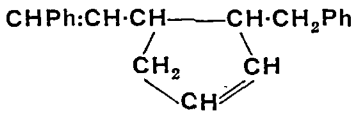
Polymerisation.—The butadienes yield spontaneously, or on heating (with or without a catalyst), dimerides and higher polymerides. So far as is known, all the artificially formed dimerides of this group, save one, are *cyclo*hexene derivatives, built up in similar fashion to the maleic anhydride derivatives mentioned above. Thus the dimeric product from isoprene appears to consist chiefly of 1:3- and 1:4-menthadiene (Wagner-Jauregg, Annalen, 1931,



488, 176), although in this example four isomeric dimerides are theoretically possible. The existence of an open-chain dimeride of isoprene, β-myrcene (supposedly

$$CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2),$$

reported by Ostromisslenski to be present in the heat-degradation product of natural rubber (J. Russ. Phys. Chem. Soc. 1915, 47, 1911, 1928) has not been confirmed. Two naturally-occurring hydrocarbons, ocimene and myrcene (*see* below), possess constitutions appropriate to open-chain dimerides of isoprene. The exception to the *cyclo*hexene rule which was noted above refers to the dimeride of α-phenylbutadiene, which according to E. Bergmann (J.C.S. 1935, 1359) has the formula



The butadienes yield either spontaneously, by the action of heat, or under the influence of such catalysts as sodium or oxygen, high polymerides which resemble in smaller or greater degree natural rubber. These appear to be long-chain compounds formed in the main by the end to end linking of the monomeric units, but not necessarily in the perfectly regular fashion attributed to natural rubber. For the constitution of these high polymerides, *see* Katz (Trans. Faraday Soc. 1935, 32, 83), Carothers, Kirby and Collins (J. Amer. Chem. Soc. 1933, 55 791); for details concerning the polymerisation of β-*n*-heptyl- and β-phenylbutadiene, *see* Carothers and Berchet (*ibid.* p. 2813); for a species of open-chain hydration-polymerisation, *see* Wagner-Jauregg (Annalen, 1931, 488, 176).

β-Chlorobutadiene (chloroprene) polymerises spontaneously to yield a rubber-like product of excellent quality, used as artificial rubber (" duprene ") (Carothers, Williams, Collins and Kirby, J. Amer. Chem. Soc. 1931, 53, 4203), and the speed of this transformation is roughly 700 times greater than that of the analogous transformation of isoprene. There are, however, four well-defined and qualitatively distinct types of polymeride:

Volatile polymeride (β) ← Chloroprene → Plastic polymeride (α)

Chloroprene ↓ Granular polymeride (ω)

Plastic polymeride (α) ↓ Non-plastic polymeride (μ)

Of these the most important are the α- and the μ polymerides or "polyprenes," since the former corresponds in its properties to unvulcanised rubber and the latter to vulcanised rubber. The μ-polymeride is the final product of the spontaneous polymerisation of chloroprene; the α polymeride is formed as an intermediate stage in the formation of the μ product, and its isolation can only be effected when (1) the temperature is not too high, since elevated temperature accelerates the transformation of α-polymeride to μ-polymeride more than it accelerates the formation of α polymeride from the monomeric diene, and (2) the reaction is not too slow, since not only do most inhibiting influences have a greater retarding effect on the formation of the α than on the μ product, but very slow reaction often yields the ω-polymeride. Light and pressure appear to have a greater accelerating effect on the formation of the α polymeride than on the transformation of this into the μ-polymeride.

The β polymeride is a dimeric terpene like material and is an undesirable by-product in rubber synthesis. The ω polymeride is also a useless product and is made up of discrete rubber-like particles which are non-plastic and not even swelled by rubber solvents; its formation is autocatalytic. When a speck of ω-polymeride appears (or is introduced) in a specimen of incompletely polymerised chloroprene, the entire specimen is soon more or less completely converted into the ω polymeride. The formation of such nuclei of the ω-polymeride is favoured by strong ultraviolet light and by metal surfaces (Carothers, Kirby, and Collins, J. Amer. Chem. Soc. 1933, 55, 789).

β Bromobutadiene (bromoprene) polymerises in a somewhat similar manner to chloroprene. μ, β, and ω polymerides have been described by Carothers, Kirby and Collins (*l.c.*, p. 793). The structures of both polychloroprene and polybromoprene are probably to be represented by the formula (X=Cl, Br):

$$—CH_2\,CH\,\underset{\displaystyle X}{\underset{|}{C}}\,CH_2\,CH_2\,CH\,\underset{\displaystyle X}{\underset{|}{C}}\,CH_2\,CH_2\,CH\,\underset{\displaystyle X}{\underset{|}{C}}\,CH_2—$$

Butadiene (erythrene, divinyl),

$$CH_2{:}CH\,CH{:}CH_2,$$

is stated to be formed in 30–50% yield by heating crotyl alcohol with toluidine hydrogen sulphate or oxalic acid; in 50–60% yield by passing crotyl acetate vapour over heated alumina; in 93% yield by passing *cyclo*butanol vapour over alumina at 300°–350°; in 60% yield by dropping αγ-dihydroxybutane on phosphoric acid heated at 300° or by passing its vapour over contact agents, heated to a suitable temperature, such as (1) dehydrated potash alum *or* aluminium sulphate or prim. potassium phosphate (E.P. 291748; 80% yield), (2) cerium phosphate on pumice, *or* a mixture of prim. sodium phosphate and graphite, with or without phosphoric acid, *or* sodium pyrophosphate and phosphoric acid (E.P. 317500; 90% yield), (3) a mixture of prim. sodium phosphate and prim. butylamine phosphate, *or* of sec. calcium phosphate, lamp black, graphite, crystalline ammonium oxalate and prim. ammonium phosphate (E.P. 326185), (4) a mixture of sec. calcium phosphate, sec. ammonium phosphate and graphite, *or* of prim. sodium phosphate, prim. butylamine phosphate, and graphite (E.P. 317500), (5) heated kaolin, (6) aluminium phosphate, and (7) anhydrous ferrous sulphate; also by passing α-butylene oxide over phosphoric acid heated at 400°–500°, and in many other ways. B.p. c. −5° to −4°; derivative with maleic anhydride, m.p. 103°–104°; derivative with α-naphthaquinone, m.p. 102°–103°; dibromides, (i) m.p. 53°, and (ii) b.p. 58°–66°/14 mm.; tetrabromides, (i) m.p. 118°, and (ii) m.p. 37°–39°.

α-Methylbutadiene, piperylene,

$$CHMe\,CH{\cdot}CH.CH_2,$$

is prepared by the dehydration of Δ^{β}-pentene-δ ol, $CHMe.CH{\cdot}CHMe(OH)$, by passing its vapour at about 20 mm. pressure over kaolin heated to 400°, or by the dehydration of βδ dihydroxypentane,

$$CHMe(OH)\,CH_2{\cdot}CHMe(OH),$$

by heating 100 g. with about 1 g. of 48% hydrobromic acid. B.p. 42.4°–42.6°/766 mm.; d_4^{20}, 0.6803; n_D^{20}, 1.4309; derivative with maleic anhydride, m.p. 62°.

β Methylbutadiene, isoprene,

$$CH_2.CMe{\cdot}CH\,CH_2,$$

can be obtained from each of three isomeric pentanes contained in American petroleum. *n*-Pentane gives on chlorination a mixture of two isomeric monochlorides (α- and β chloropentane) which yields on dehydrochlorination with quicklime at 385°–400° a mixture of Δ^{α}- and Δ^{β} pentene. The latter, when passed over alumina heated to 450°, suffers conversion into trimethylethylene, from which dichloro*iso*pentane, $CMe_2Cl\,CHCl\,CH_3$, may be obtained either by direct addition of chlorine, or by addition of hydrogen chloride (yielding *iso*amyl chloride, $CMe_2Cl\,CH_2{\cdot}CH_3$) followed by chlorination. The dichloro*iso*pentane thus obtained yields isoprene when passed over heated barium chloride.

*iso*Pentane, $CHMe_2{\cdot}CH_2{\cdot}CH_3$, gives on chlorination the chlorides $CMe_2Cl\,CH_2{\cdot}CH_3$ and $CHMe_2{\cdot}CHCl{\cdot}CH_3$, each of which yields trimethylethylene almost quantitatively when passed over quicklime at 450°. From the trimethylethylene isoprene is obtained as above.

Tetramethylmethane gives on chlorination the chloride $CMe_3{\cdot}CH_2Cl$, which isomerises to *iso*amyl chloride, $CMe_2Cl\,CH_2\,CH_3$, on distillation. The latter may be converted into dichloro*iso*pentane and thence into isoprene as above. For laboratory purposes isoprene can be prepared by thermal degradation of rubber (Bassett and Williams, J.C.S. 1932, 2324) or by thermal degradation of limonene using Harries and Gottlob's "isoprene lamp" (Annalen, 1911, 383, 228; *see also* Whitby and Crozier, Canad. J. Res. 1932, 6, 203).

Crude isoprene can be freed from hydrocarbon impurities by converting into its hydrobromide, $CMe_2{\cdot}CH\,CH_2Br$, and thence by the action of 5% potassium carbonate into the tertiary alcohol, $CMe_2(OH)\,CH{:}CH_2{\cdot}$ from this the pure hydrocarbon is obtained by heat-

ing with a little aniline hydrobromide (Farmer and Warren, J.C.S. 1931, 3221). An alternative method of purification consists in forming the crystalline sulphone derivative of the hydrocarbon by the action of sulphur dioxide, and decomposing this compound by heat (Jones and Williams, J.C.S. 1934, 829). Another method of purification which, it is claimed, gives a very pure product relies entirely on fractional distillation of the crude hydrocarbon using a vacuum-jacketed column (140 cm. long) and a reflux ratio of 15 : 1 (Bekkedahl, Wood and Wojciechowski, J. Res. Nat. Bur. Stand. 1936, **17**, 883). Isoprene has b.p. 34·076°/760 mm.; d_4^{20}, 0·6805; n_D^{20}, 1·4160; derivative with maleic anhydride, m.p. 63°–64° (Bekkedahl, Wood and Wojciechowski, *l.c.*; Farmer and Warren, *l.c.*).

αα-Dimethylbutadiene, $\mathrm{CMe_2:CH\cdot CH:CH_2}$. A hydrocarbon which appears to be substantially pure αα-dimethylbutadiene has been prepared from β-*cyclo*propylpropene by the successive action of hydrobromic acid and alcoholic potash (Keersbilck, Bull. Soc. chim. Belg. 1929, **38**, 205; Farmer and Warren, J.C.S. 1931, 3231). Mixtures of αα- and αγ-dimethylbutadiene are obtained by dehydration of various alcohols, *e.g.* $\mathrm{CHMe:CH\cdot CMe_2\cdot OH}$ (5% αα-) and $\mathrm{CMe_2:CH\cdot CHMe\cdot OH}$ (small proportion αα-), but satisfactory separation of the components has not been achieved (Bacon and Farmer, J.C.S. 1937, 1065). B.p. 72·6°–76·6°/758 mm.; d_4^{20}, 0·7183; n_D^{20}, 1·4525; derivative with maleic anhydride (highly polymerised substance), decomposes without melting.

αβ-Dimethylbutadiene,

$$\mathrm{CHMe:CMe\cdot CH:CH_2},$$

is prepared from γ-methyl-Δ^{β}-penten-δ-ol, $\mathrm{CHMe:CMe\cdot CHMe(OH)}$, either by the successive action of hydrochloric acid and quinoline (Abelmann, Ber. 1910, **43**, 1583) or by direct dehydration (Farmer and Warren, J.C.S. 1931, 3232). B.p. 76·0°–79·4°/773 mm.; d_4^{20}, 0·7279; n_D^{20}, 1·4511; derivative with maleic anhydride, m.p. 67°.

αγ-Dimethylbutadiene,

$$\mathrm{CHMe:CH\cdot CMe:CH_2},$$

is prepared by the dehydration of β-methylpentane-βδ-diol,

$$\mathrm{CMe_2(OH)\cdot CH_2\cdot CHMe(OH)}$$

(Kyriakides, J. Amer. Chem. Soc. 1914, **36**, 994; Farmer and Scott, J.C.S. 1930, 511); a small proportion of the isomeric αα-dimethylbutadiene is formed at the same time (Bacon and Farmer, unpublished work) but this hydrocarbon does not constitute the main product as supposed by Whitby and Gallay (Canad. J. Res. 1932, **6**, 280). B.p. 75·6°–75·7°/762 mm.; d_4^{20}, 0·7196; n_D^{20}, 1·4467; derivative with maleic anhydride, m.p. 56°–57°; dibromide, oil, b.p. 101°–103°/22 mm. (decomp.).

αδ-Dimethylbutadiene,

$$\mathrm{CHMe:CH\cdot CH:CHMe},$$

is prepared by the dehydration of ethyl propenyl carbinol, $\mathrm{CHMe:CH\cdot CH(OH)Et}$, at 15–20 mm. pressure in the presence of kaolin at 420° (Kyriakides, J. Amer. Chem. Soc. 1914, **36**, 994). B.p. 77·0°–81·6°/765 mm. The wide range of boiling-point is probably due partly to the presence of *cis-trans*-isomerides, but partly also to the presence of a very small proportion of α-ethylbutadiene. The lower boiling fraction of the hydrocarbon gives the values: d_4^{20}, 0·7108; n_D^{20}, 1·4427; and the higher boiling fraction: d_4^{20}, 0·7152; n_D^{20}, 1·4493. Derivative with maleic anhydride, m.p. 95°–96°; dibromide, b.p. 85°/11 mm.

βγ-Dimethylbutadiene or *diisopropenyl*,

$$\mathrm{CH_2:CMe\cdot CMe:CH_2},$$

is prepared by the dehydration of pinacol, $\mathrm{CMe_2(OH)\cdot CMe_2(OH)}$, by heating with a little hydrobromic acid (Kyriakides, J. Amer. Chem. Soc. 1914, **36**, 987). B.p. 69·0°/761 mm; d_4^{20}, 0·7262; n_D^{20}, 1·4393; derivative with maleic anhydride, m.p. 78°–79°; dibromides (i) m.p. 47°, (ii) oil, b.p. 101°–105°/15 mm.

Myrcene,

$$\mathrm{CMe_2:CH\cdot CH_2\cdot CH_2\cdot C(:CH_2)\cdot CH:CH_2},$$

occurs in bay oil, the essential oil of hops, *Barosma venusta*, and the oil of *Lippia citriodora*. It is formed, together with other hydrocarbons, by the action of potassium bisulphate on likare oil. It is a colourless liquid, b.p. 62°–63°/17 mm., which polymerises on long standing, and yields myrcenol on hydration with a mixture of sulphuric and acetic acid; d^{15}, 0·8013; n_D^{19}, 1·4700; derivative with maleic anhydride, m.p. 34°–35°.

Ocimene,

$$\mathrm{CH_2:CMe\cdot CH_2\cdot CH_2\cdot CH:CMe\cdot CH:CH_2},$$

occurs in the leaves of *Ocimum basilicum*.

β-Myrcene, formerly reported to possess an open-chain structure, is without doubt a cyclic compound (see *Polymerisation*, above).

β-Chlorobutadiene, chloroprene,

$$\mathrm{CH_2:CCl\cdot CH:CH_2},$$

is prepared by the addition of hydrogen chloride to vinylacetylene (*see* olefin-acetylenes). The primary addition product is chloromethylallene, but this isomerises spontaneously, especially in the presence of cuprous chloride, into chloroprene (Carothers, Berchet and Collins, J. Amer. Chem. Soc. 1932, **54**, 4066; Carothers, Williams, Collins and Kirby, *ibid.* 1931, **53**, 4203):

$$\mathrm{CH_2:CH\cdot C:CH} \xrightarrow{\mathrm{HCl}} \mathrm{CH_2Cl\cdot CH:C:CH_2} \xrightarrow[\alpha\gamma\text{- change}]{} \mathrm{CH_2:CH\cdot CCl:CH_2}.$$

B.p. 59·4°/760 mm.; d_4^{20}, 0·9563; n_D^{20}, 1·4583; it yields no derivatives with maleic anhydride or α-naphthaquinone.

β-Bromobutadiene, bromoprene,

$$\mathrm{CH_2:CBr\cdot CH:CH_2},$$

is prepared by the action of concentrated hydrobromic acid on vinylacetylene in presence

of freshly prepared cuprous bromide (Carothers, Collins and Kirby, J. Amer. Chem. Soc. 1933, 55, 786).

$$CH_2{:}CH\,C{:}CH \xrightarrow{HBr} CH_2Br{\cdot}CH.C{:}CH_2 \longrightarrow CH_2\,CH{\cdot}CBr{:}CH_2$$

B p. 42–43°/165 mm.; d_4^{20}, 1·397; n_D^{20}, 1·4988; derivative with maleic anhydride (hydrated), m p. 186 5°–187°; derivative with α-naphthaquinone, m.p. 138°.

Other open-chain butadienes.—The following compounds, *inter alia*, have been obtained:

	B p (M p) (°C.)	M.p of maleic anhydride derivative (°C).	M p of naphthaquinone derivative(°C)
β n Butyl-	121–123	—	63–64
β-*tert.*-Butyl-	104–106	124	90
β-*n*-Heptyl	52–54 (5 mm.)	—	81
α-Phenyl-	96 (18 mm.)	120	—
β-Phenyl-	60–61 (17 mm.)	105	146–147
α-Methyl β chloro-	99 5–101	—	181
α Ethyl β chloro-	68·2–69 (117 mm.)	—	151–152
βγ-Dichloro-	98	—	—
βγ-*tert.*-Butyl	168–170	128–129	—
αδ-Diphenyl- (3 forms)	(152); (70); oil	207	—
βγ-Diphenyl-	(49)	—	—
αδ-Dibenzyl-	(79)	—	—
ααγ-Trimethyl-	92	—	—
ααδ- „	97–99	—	—
αβγ- „	33–34 (7 mm.)	—	—
αδ-Dimethyl βγ-diethyl-	158–165	90–91	91–92
αβγδ-Tetramethyl-	132–134	—	—
αβγδ-Tetraphenyl-	(183–184)	—	—
ααδδ- „	(202)	—	—

Hexatriene, $CH_2{\cdot}CH\,CH{:}CH\,CH.CH_2$, is prepared by treating *s* divinylethylene glycol, $CH_2{\cdot}CH{\cdot}CH(OH)\,CH(OH){\cdot}CH.CH_2$, with phosphorus tribromide and dehalogenating the product with zinc (van Romburgh and Muller, Proc. K. Akad. Wetensch Amsterdam, 1914, 16, 1090). It is a colourless liquid, b p. 80°–80 5°; $d_4^{13.5}$, 0 740; $n_D^{13.5}$, 1·5172; derivative with maleic anhydride, m p 51 5°. For *cis*-hexatriene and for the dibromides of hexatriene, *see* Farmer, Laroia, Switz and Thorpe, J.C.S. 1927, 2937.

For αζ dimethylhexatriene and αζ diphenylhexatriene (m.p. 124°–125°), *see* Farmer, Laroia, Switz and Thorpe (*l c.*), and Kuhn and Winterstein (Helv. Chim. Acta, 1928, 11, 87).

Higher Polyenes.—The following series of αω diphenyl-polyenes, $Ph\,[CH.CH]_n{\cdot}Ph$, has been synthesised by Kuhn and Winterstein, *l c.*:

αθ-diphenyl-octatetraene, m p. 232°.
ακ „ decapentaene, m.p. 253°.
αμ „ dodecahexaene, m.p. 267°.
αρ „ hexadecaoctaene, m.p. 285°.

For the addition products of these, *see* Kuhn and Winterstein, *l.c*, pp. 123, 144. E. H. F.

BUTADIENES AND POLYOLEFINS (Non-conjugated). The non-conjugated butadienes are allenes (*q.v.*). Of the non-conjugated polyolefins the most important compounds are the symmetrical diolefins obtained by the action of sodium on halogeno-olefins of the type $R{\cdot}CH{:}CH{\cdot}CH_2I$ or $R'{\cdot}CH{:}CR''{\cdot}CH_2I$ (R = H or alkyl). Unsymmetrical diolefins are formed by dehalogenation and elimination reactions similar to those employed for the butadienes (*q.v.*).

The diolefins unite with one or two molecules of chlorine, bromine, hypochlorous acid and other olefinic reagents; they readily undergo catalytic hydrogenation and are converted by dilute sulphuric acid into olefinic oxides; they are susceptible of oxidation by atmospheric oxygen and frequently polymerise spontaneously.

Diallyl ($\Delta^{\alpha\epsilon}$ hexadiene),

$$CH_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH.CH_2,$$

b p. 59 3°/769 mm., is obtained from allyl iodide and sodium; *dicrotyl* ($\Delta^{\beta\zeta}$-octadiene),

$$CHMe\,CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH\,CHMe,$$

b p. 117°–119°, is obtained from crotyl bromide and sodium; *di isocrotyl* (βε-dimethyl $\Delta^{\alpha\epsilon}$-hexadiene), $CH_2{\cdot}CMe\,CH_2{\cdot}CH_2{\cdot}CMe\,CH_2$, b.p. 113°–114°, is obtained from *iso*crotyl bromide and sodium. E. H. F.

BUTALDEHYDES, C_4H_8O.

Normal butaldehyde, $CH_3{\cdot}[CH_2]_2{\cdot}CHO$, is prepared by distilling a mixture of calcium *n* butyrate, calcium formate and iron filings The distillate is fractionated, and the product isolated as the bisulphite compound from the fraction boiling at 70°–110° (Lipp, Annalen, 1882, 211, 355; Linnemann, *ibid.* 1872, 161, 186; Kahn, Ber. 1885, 18, 3364). It can also be prepared by the action of magnesium *n*-butyl bromide on ethyl orthoformate (Bodroux, Compt. rend. 1904, 138, 700), by catalytic hydrogenation of crotonaldehyde (B.P. 271103, 147118) and by passing the vapour of *n* butyl alcohol over heated copper oxide (B.P. 173004)

It is a liquid of b p. 73°–74° and d_4^{20} 0 8170 (Bruhl, Annalen, 1880, 203, 18). It dissolves

in water to the extent of 3·7 parts in 100. It yields a crystalline bisulphite compound (Juslin, Ber. 1884, **17**, 2505), and with aqueous ammonia at 0° gives butaldehyde-ammonia, $C_4H_{11}ON,3\frac{1}{2}H_2O$, m.p. 30°–31° (Guckelberger, Annalen, 1847, **64**, 52). If alcoholic ammonia and the aldehyde are allowed to stand for a month and then heated for a day at 100°, two bases are formed, tetrabutyraldine, and dibutyraldine, $C_8H_{17}ON$, which can be isolated by distilling off the unchanged starting materials and fractionally precipitating with platinic chloride. The latter base only has been crystallised.

Butaldehyde is used for the preparation of butyric acid, and for increasing the elasticity and toughness of rubber used for dipping (U.S.P. 1445080). Its condensation products are used as vulcanisation accelerators.

On standing four days with a little zinc chloride, butaldehyde polymerises to *parabutaldehyde*, $(C_4H_8O)_3$, an oil of suffocating smell, b.p. 129°–130°/35 mm., and d^{21} 0·917 (U.S.P. 1576503). It remains liquid at −20°. On distilling or heating with acids it yields butaldehyde and resinous compounds.

Metabutaldehyde, $(C_4H_8O)x$, is formed, with parabutaldehyde by the action of hydrogen chloride on butaldehyde at −20° (Franke and Wozelka, Monatsh. 1912, **33**, 353). It forms needles of m.p. 173°, subliming at 150°, readily soluble in hot alcohol and benzene but not in water. Its molecular weight is about 250.

ββγ-Trichlorobutaldehyde (butyl chloral), b.p. 164°–165°/750 mm., and its hydrate, m.p. 78°, have been prepared by Pinner (Annalen, 1875, **179**, 26).

iso*Butaldehyde*, $(CH_3)_2CH{\cdot}CHO$, is prepared by the oxidation of *iso*butyl alcohol with potassium dichromate (Lipp, Annalen, 1880, **205**, 2; Pfeiffer, Ber. 1872, **5**, 699; Fossek, Monatsh. 1881, **2**, 614; 1883, **4**, 661) or by distilling calcium formate with calcium *iso*butyrate (Linnemann and Zotta, Annalen, 1872, **162**, 7). It is a liquid of b.p. 63°–64°/757 mm. (Brühl, Annalen, 1880, **203**, 18), d_4^{20} 0·7938 (Brühl) and d^{15} 0·79722 (Perkin, J.C.S. 1884, **45**, 476). It dissolves in 9 parts of water at 20° and is soluble in alcohol and ether. Condensation compounds have been obtained by Perkin (J.C.S. 1883, **43**, 91).

Diisobutaldehyde, $(C_4H_8O)_2$, b.p. 136°–138°/18 mm., is obtained by heating *iso*butaldehyde with a concentrated solution of sodium acetate at 150° (Fossek, *l.c.*).

Paraisobutaldehyde, $(C_4H_8O)_3$, m.p. 59°–60°, b.p. 195·2°/752·3 mm., is obtained by the action of zinc chloride on the aldehyde (Fossek, *l.c.*); also by the action of chlorine or of bromine or iodine vapour (Barbaglia, Ber. 1872, **5**, 1052; 1873, **6**, 1064; Gazzetta, 1886, **16**, 431) on the aldehyde.

BUTANE AS A FUEL. Liquefied petroleum gases, *e.g.* propane and butane, are finding an ever-increasing market both as a domestic fuel supplied in containers, and as industrial fuel, *e.g.* for cooking in railway dining-cars, for general industrial heating, and, to a very much smaller extent, as a fuel mixed with hydrogen for airships.

The potential supply of butane is so great as 40,000 tons a year, a good deal of which finds its way into ordinary motor spirit, where it is advantageous as a means of increasing volatility and for increasing anti-knock value.

The propane supplies are even greater and amount to approximately 70,000 tons a year.

The method of extracting these gases consists in absorption from natural gas by means of a convenient solvent, recovery by means of distillation and then careful fractionation. A certain amount of chemical treatment is necessary and a convenient desulphurising agent is sodium or calcium hypochlorite.

Some properties of liquid propane and butane follow:

Property.	Commercial Propane.	Commercial Butane.
Specific gravity of liquid	0·51	0·58
Initial boiling-point	−51°F.	15°F.
Cu. ft. of gas at 60°F. and atmospheric pressure per gallon of liquid at 60°F.	36·3	31·5
Percentage of the gas in air for maximum temperature of flame	4·3	3·3

In the case of propane the liquid vapourises conveniently at ordinary temperatures, but it is sometimes necessary in the case of butane to provide auxiliary heat.

For domestic use cylinders are provided holding 60 days' normal fuel supply.

A variety of industrial uses is as follows:

(1) Direct liquefied gas serves for domestic and industrial uses.

(2) Enrichment of low thermal standard gas, *e.g.* water gas.

(3) Raw material for reforming to ordinary town gas services.

(4) Special purposes, *e.g.* solvents, cleansing mineral oils, refrigeration, source of synthetic chemicals, welding and metal cutting.

A. E. D.

BUTANE *v.* Butyl- compounds.

BUTANONE (*Methyl ethyl ketone*) *v.* Acetone Oil.

BUTEA FRONDOSA. The *Butea frondosa*, also called *Dhak* or *Pulas*, is a fine tree, 30–40 ft. high, belonging to the order *Leguminosæ*. It is common throughout India and Burma and is found in the North-West Himalaya as far as the Jhelum River. The flowers, which in the dried condition are known as tísu, késú, kesuda, or palás-képpúl, have a bright-orange colour, and, although they are much larger, closely resemble in appearance the common gorse-flower (*Ulex europæus*), with which, indeed, they are botanically allied.

From the *Butea frondosa* is also obtained the so-called "Butea gum" or "Bengal kino," employed by the natives for tanning leather; and the tree is of additional interest because in many parts of India the lac insect (*Coccus lacca*) is reared upon it. This latter, as is well known,

causes the formation of stick lac from which shellac and lac dye are prepared.

Butin.—The flowers are extracted with boiling water and the extract digested with a little sulphuric acid. A light viscous precipitate devoid of dyeing property separates and this is removed while hot and the filtrate left overnight. The clear liquid is now decanted from a small quantity of tarry substance and partially evaporated on the water bath. A further quantity of a black viscous precipitate thus separates, and when this has been removed the filtrate, after some days, deposits crystals of the colouring principle, *butin.* For purification the product is dissolved in a little alcohol, the mixture poured into ether, and the solution well washed with water. The ethereal liquid is evaporated and the residue repeatedly crystallised from dilute alcohol (Perkin and Hummel, J.C.S. 1904, 85, 1459)

Butin, $C_{15}H_{12}O_5+\frac{1}{2}H_2O$, colourless needles *(from alcohol), m p. 224°–226°, $+2H_2O$, pale* yellow needles (from water), dissolves in alkaline solutions with a pale orange red tint, and gives with alcoholic lead acetate a faintly yellow, almost colourless, precipitate. The *triacetyl* derivative, colourless leaflets, melts at 123°–125°, and the *tribenzoyl* compound, colourless needles, at 155°–157°. On fusion with alkali at 200°–220° butin gives protocatechuic acid and resorcinol.

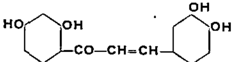
When butin is boiled with dilute potassium hydroxide solution the pale-coloured liquid becomes much darker, and on acidifying an orange crystalline precipitate separates which consists of *butein.*

Butein, $C_{15}H_{12}O_5,H_2O$, needles, melts at 213°–215°; dissolves in alkaline solutions with a deep orange-red colour, and with alcoholic lead acetate gives a deep red precipitate. *Tetra acetylbutein,* pale yellow needles, melts at 129°–131°.

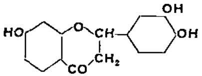
When fused with alkalis butein gives resorcinol and protocatechuic acid, whereas by the action of boiling 50% potassium hydroxide solution, protocatechuic acid and resacetophenone are produced.

By methylation with methyl iodide butin gives *butin trimethyl ether,* colourless plates, m p. 119°–121°, and also *butein trimethyl ether, yellow leaflets, m.p. 156°–158°. In a similar* manner, butein yields not only butein trimethyl ether, but also butin trimethyl ether.

Perkin and Hummel thus assigned the chalkone structure (I) to butein and the corresponding flavanone configuration (II) to

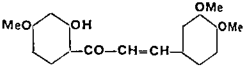


I.



II.

butin, and established the correctness of these formulæ by the synthesis of butein and butin trimethyl ethers. Resacetophenone monomethyl ether condensed with veratraldehyde yields butein trimethyl ether (III), and this, when digested with boiling dilute alcoholic sulphuric acid gives butin trimethyl ether (IV).



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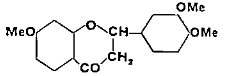
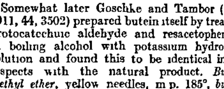


IV.

Somewhat later Goschke and Tambor (Ber. 1911, 44, 3502) prepared butein itself by treating protocatechuic aldehyde and resacetophenone in boiling alcohol with potassium hydroxide solution and found this to be identical in all respects with the natural product. *Butein methyl ether,* yellow needles, m p. 185°, *butein 3′-4′-dimethyl ether,* yellow prisms, m p 203°, and *butein tetramethyl ether* (Ber. 1912, 45, 186) colourless needles, m.p. 89°, were also described

A further synthesis of butein is recorded by Shinoda, Sato and Kawagoye (J. Pharm. Soc. Japan, 1929, 49, No. 571, 123). The condensation of the acid chloride of dicarbethoxycaffeic acid with resorcinol in dry nitrobenzene-ether solution in presence of aluminium chloride at 100° furnishes a product which, when heated with 10% potassium hydroxide solution in an atmosphere of hydrogen, yields butein on acidification.

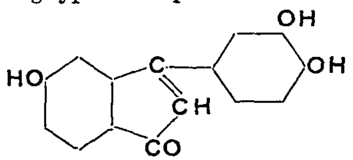
Butein itself is also converted into butin by means of dilute alcoholic sulphuric acid, and the butin can again be transformed into butein by the action of potassium hydroxide solution With alcoholic potash butin trimethyl ether also gives butein trimethyl ether, and these changes are readily explained if it is assumed that the *intermediate compound*



or its trimethyl ether is the first product of the reaction in each case, and that this subsequently, by loss of water, passes into either chalkone or flavanone, or both.

When butein dissolved in acetic acid is treated with a few drops of sulphuric acid, and the solution is boiled, a new substance gradually separates in the form of crystals, which possess a beetle green iridescence, and dissolve in alkaline solutions with a deep blue colour. The acid liquid decanted from the crystals, on dilution with water, gives a brown precipitate

soluble in alkalis with a bluish-violet coloration, which dyes mordanted calico shades of a similar character to those yielded by anthragallol. It appears probable that this more soluble substance represents the first product of the reaction, and is subsequently converted into the green iridescent compound. A consideration of the formula of butein renders it unlikely that these new substances are anthraquinone derivatives; on the other hand, it is suspected that by loss of water ring formation takes place and that an indone derivative of the following type is first produced:



Butin and butein dye mordanted woollen cloth identical shades, though as butin gives with an alcoholic lead acetate solution a practically colourless precipitate, it is not to be regarded as a colouring matter. In other words, butin is merely a colouring principle and is converted during the dyeing operation by the action of the mordant into the colouring matter butein. With chromium, aluminium, tin and iron mordants reddish-brown, brick-red, full yellow and brownish-black shades respectively are obtained, and these are strikingly similar to those yielded by some of the hydroxybenzylidenecoumaranones artificially prepared by Friedländer and Rüdt (Ber. 1896, **29**, 879).

The butea flowers contain only a trace of free butin or butein, and the glucoside present, which has not yet been isolated, is probably that of butin. In dyeing operations the glucoside is first hydrolysed by boiling the flowers with dilute hydrochloric or sulphuric acid and the acid neutralised with sodium carbonate; on evaporation a material is obtained which readily dyes by the usual methods. Such products give the following shades: with chromium, deep terracotta; with aluminium, a bright orange; with tin, bright yellow, and with iron, a brownish-olive. The chromium colour is characteristic and is much redder in tint than that yielded by any known natural yellow dye.

A. G. P. and E. J. C.

BUTESIN. *n*-Butyl *p*-aminobenzoate, $H_2N{\cdot}C_6H_4{\cdot}CO_2Bu$, it is used in the form of a dusting powder or ointment as a local anæsthetic. (Abbott, Chicago; Pharmaceutical Products, London.) B.P.C.

BUTOLAN. Carbamic acid-ester of *p*-hyoxydiphenylmethane. Brand of Carphenol. Vermifuge.

BUTOXYL. Cellulose lacquer solvent, is the acetate of 1:3-butyleneglycol ether. Insoluble in water (J. Oil Col. Chem. Assoc. 1935, 222).

BUTTER. Butter is the fatty food substance prepared from the milk of mammals by heating or churning the milk, or the cream which has been first separated from the milk, either in a sweet condition or after suitable ripening. In practice, cream is now almost generally employed, but milk was at one time, and in some parts still is, directly used. Butter prepared for sale in this country is the product of the milk of the cow, but in some countries butter is made from the milk of other mammals, e.g. goats, buffaloes and sheep.

The description "butter" is also in usage to express similarity to butter in appearance or consistency of some other substances which have no connection with genuine butter, for example, vegetable butter, coconut butter, cocoa (cacao) butter, butter of antimony.

Definition of butter and legal restrictions relating thereto in this country.—The legal definition of butter in this country is—"Butter is the substance usually known as butter, made exclusively from milk or cream, or both, with or without salt or other preservative, and with or without the addition of colouring matter" (Food and Drugs (Adulteration) Act, 1928, s. 24). This definition is modified by the Public Health (Preservatives in Food) Regulations, 1925 (S. R. & O. 1925, 775) which do not permit the use of any preservative in butter, and prohibit the use of certain colours in any food. For the purpose of these regulations, common salt is not regarded as a preservative. The colouring matters prohibited in food are picric acid, Victoria yellow, Manchester yellow, aurantia, aurine, gamboge, and metallic colours.

"Premises on which by way of trade butter is blended, re-worked, or subjected to any other treatment but not so as to cease to be butter," must be registered (Food and Drugs (Adulteration) Act, 1928, s. 8).

The regulations as to the maximum amount of water in butter are of a two-fold character: (1) The Sale of Butter Regulations, 1902, provide that where the proportion of water exceeds 16% it shall be presumed that the butter is not genuine. This presumptive standard applies only to butter, e.g. farm and creamery butter, which has not gone through any process such as blending or reworking subsequent to manufacture. (2) The Food and Drugs Act (*l.c.* ss. 12 & 11) fixes an absolute limit of 16% of water for imported butter, and for butter which has undergone any process in a butter factory.

The retail sale of butter comes under the provisions of the Sale of Food (Weights and Measures) Act, 1926, particularly as to the weight of paper that may be included in a sale by retail.

The Food and Drugs Act (*l.c.*) also defines (s. 34) the article known as "milk-blended butter," and limits the amount of water which it may contain to 24% (*l.c.* s. 11). The manufacture of milk-blended butter has, however, practically, if not wholly, ceased.

No limits have been fixed as to the amount of fat or of curd in butter for sale in this country, but the Minister of Agriculture has power under the Food and Drugs Act (*l.c.* s. 7) to make a presumptive limit of the proportion of any milk-solid other than milk fat in genuine butter.

PREPARATION.

Butter is obtained from milk or cream by churning, a process which has been used from

time immemorial All the numerous types of churns used in modern butter-making arise from the development of the primitive skin bag in which milk was rolled, or the wood box in which milk was beaten, and in later days enclosed and rotated

Cream, freshly separated from milk and in a sweet condition, may be directly employed for churning. More generally, cream is allowed to sour or ripen naturally, as in common farm practice, or is cultivated for a brief period with a "starter"—a culture of lactic acid bacteria and associated species capable of developing butter flavour and aroma. Naturally ripened cream, the oldest method, is open to development of adventitious germs with production of unwanted flavour or aroma.

Where a "starter" is employed, the cream after separation from milk and before addition of the "starter" is pasteurised to destroy germs of milk borne diseases and ferments which may affect the quality or character of the butter There are various methods of pasteurisation and subsequent cooling of the cream. After addition of the "starter" the cream is maintained at a temperature of 18° to 21° for some hours before churning Butter may be produced without regard to the acidity of the ripened cream, but if the acidity exceeds about 0 3% as lactic acid it is preferable to reduce it to an amount below 0 3% by suitable treatment before the cream is passed to the churn.

The temperature at which the churning is carried out is an important factor It must be high enough to enable the fat particles to cohere, but not so high as to give a greasy butter. If too low the cream will be merely "whipped." In hand churns a suitable temperature is 12 5° to 15·5°, in creamery churns it may be somewhat lower. Churning is carried out at a higher temperature in winter than in summer Before commencement of churning, colouring matter is added, if, as is usually the case, butter of a standard tint is required The most suitable butter fat content of cream for churning is from 30 to 33%.

Churning consists essentially in beating or shaking the cream (or milk) in such conditions *that the minute fat globules under the concussion* brought about by vigorous agitation coalesce, producing at first small granules and then larger aggregates, which, if churning is continued, collect together into one mass. Farm churning was at one time almost generally carried to this final stage, but the difficulty of washing or working out enclosed buttermilk from such a mass has led to improved methods.

A churn is so constructed that by means of various devices such as eccentric rotatory motion and the provision of obstacles within the churn, the liquid undergoes violent shaking and beating. After operating for a brief period, air and gases are liberated through a vent, and the churning continued until a change manifests itself within the churn by the increasing load on its movement, more power being necessary to continue the churning; by a change in the sound of the splash; and by the clearing of the cream from the spy-glass of the churn. This change is known as the "coming" of the butter, and generally takes place in normal conditions about 35 to 50 minutes from the commencement of churning. When the butter aggregates have attained a size that will enable them to be strained from the non-fatty serum or buttermilk the latter is run off. The granules are then sprayed with water which is allowed to drain away, or the churn is closed, water added, and the whole agitated to remove as much as possible of the adhering serum. The washing water is drained away, and the butter worked into a uniform mass either within the churn or on a table.

If a heavily salted butter is being made, the salt is added at this stage and worked thoroughly into the butter; in the case of a lightly salted butter with less than about 2% of salt, it is preferable to add the salt as a brine solution while the butter is in the granulated state.

Various views are held as to the causes for the change in milk fat during churning. The earlier theories of a protective membrane round each globule and its rupture in churning are still held by some but in a modified form. Rahn (Milch. Forsch 1926, 3, 512) states that each globule of fat is surrounded by a thin layer of protein. Fischer and Hooker ("Fats and Fatty Degeneration," Wiley, 1917) suggest an emulsion theory. in milk and cream, fat constitutes the dispersed phase, and skim-milk or hydrated colloid emulsion the continuous phase; in butter these phases are reversed. The permanence of the fat globules as individual units is attributed to surface tension, and to adsorption on the globular surface of some of the constituents of skim-milk, and possibly also to viscosity of milk.

Rogers and associates ("Fundamentals of Dairy Science," Reinhold Publishing Corpn, 1935) suggest that the continued agitation of cream at favourable temperatures results in the initiation and growth of clumps of fat, and when the ratio of surface area of clumps to cubic content becomes relatively small the emulsion breaks and the fat gathers in a plastic mass (butter). The fat phase is, however, not continuous in a strict sense but exists in form of globules.

Possibly something in each of these theories is *necessary to the solution of the* problem Churning ruptures any adsorbed or viscous layer on the surface of the fat globules enabling them to coalesce and form a more or less solid mass of butter fat into which have been emulsified small divided droplets of hydrated colloid (buttermilk). Rogers and others (*l c.*) suggest that the constancy of ratio of water to fat in butters churned under identical conditions indicates that there is a definite surface relationship between water droplets and fat globules.

Composition of Butter.

Butter consists mainly of fatty glycerides derived from milk and usually spoken of as "butter fat" or "milk fat," together with water, and small quantities of proteins, lactose, and mineral matter, classed together as "curd" In addition, butter contains certain vitamins, natural colour, and some other substances associated with the fat. Butter as sold usually

contains added colouring matter, and salt butter contains added common salt.

The following table summarises some of the numerous results giving the average percentage composition of butter according to various authorities (Elsdon, "Edible Oils and Fats," Benn, London, 1926, 433).

	Storch.		Mitchell.	Parry.
	From fresh cream.	From ripened cream.		
Fat	83·75	82·97	84–87	86·8
Water	13·03	13·78	12–14	12·0
Protein	0·64	0·84	0·75	0·5
Lactose	0·35	0·39	—	0·45
Ash	0·14	0·16	0·60	0·25
Salt	2·09	1·86	—	—
Lactic acid	—	—	0·50	—

1. **Water.**—The quantity of water in butter depends upon various details within the control of the manufacturer, and it has therefore become necessary in this as in other countries to fix maximum limits for water. The basis for the limit adopted in this country was the inquiry made by the Departmental Committee on Butter Regulations (Report, 1903) which considered that it was not necessary for well-made butter, excluding Irish Salt Firkin butter, to contain more than 16%. The usual range of water since the limit was fixed is from 12 to 15%.

2. **Butter fat.**—This is the chief constituent of butter, being present in unsalted butter prepared for sale in this country to the extent of 83 to 85%. On gently heating butter, the fat melts and separates from the aqueous curdy matter. After allowing the water and curd to settle, the fatty layer is passed through a dry filter paper using a hot funnel, and the fat obtained as a clear oil, usually of a yellow colour, but sometimes almost colourless, setting to a granular crystalline mass. This fat consists of glycerides of fatty acids, together with the characteristic fat-soluble vitamins A and D, the natural or added colouring matter of the butter, and some unsaponifiable matter, e.g. cholesterol associated with the fat.

Composition of the Fat.—The glycerides of butter fat contain all the saturated fatty acids of even number of carbon atoms from C_4 to C_{18} (butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic) as well as the unsaturated C_{18} acid (oleic). In addition to these well-recognised constituents, other acids have been recorded as being present. Browne (J. Amer. Chem. Soc. 1899, **21**, 613) recorded the presence of *di*hydroxystearic acid; Hilditch and Jones (Analyst, 1929, **54**, 73) conclude that butter fat contains small quantities of the C_{20} saturated acid (arachidic), as well as linoleic acid and possibly traces of linolenic acid; Ekstein (J. Biol. Chem. 1933, **103**, 135) also finds linoleic and linolenic acids; and Bosworth and Brown (*ibid.* 1933, **103**, 115) have identified in butter fat the saturated acids (lignoceric, behenic) and unsaturated acids (decenoic, tetradecenoic). Bosworth and Helz (J. Biol. Chem. 1935, **112**, 489) find monohydroxypalmitic acid, and (*ibid.* 1936, **116**, 203) cerotic acid in butter fat.

The proportions in which the acids exist as glycerides in the fat have frequently been the subject of inquiry. (For the earlier work on this part of the subject, *see* Hehner and Angell, "Butter: its Analysis and Adulterations," Churchill, 1877; Bell, "Chemistry of Foods," Chapman and Hall, 1883; and Browne, J. Amer. Chem. Soc. 1899, **21**, 807).

Crowther and Hynd (Biochem. J. 1917, **11**, 139), and Holland and others (J. Agric. Res. 1916, 101; *ibid.* 1918, 719; *ibid.* 1923, 365) effected separation of the fatty acids by esterification and fractional distillation. Hilditch and Jones (Analyst, 1929, **54**, 75) removed the lower fatty acids and fractionated them by distillation as free acids, and separated the non-volatile acids into two groups, by means of the soluble and insoluble lead salts respectively. The acids recovered from these two groups were converted into methyl esters and fractionally separated. The results have been substantiated by Hilditch and Sleightholme (Biochem. J. 1930, **24**, 1105) and by Dean and Hilditch (*ibid.* 1933, **27**, 889).

The results are given below, as weight percentages on the separated fatty acids:

	Hilditch and Jones. 3 New Zealand Butters.			Hilditch and Sleightholme.				
	A	B	C	Autumn fed.	Coconut cake.	Soya cake.	Early summer.	Pasture fed.
Butyric	3·4	3·1	3·2	3·1	3·4	3·6	3·3	3·5
Caproic	1·8	1·9	1·7	1·7	2·0	1·5	1·3	1·7
Caprylic	0·9	0·8	0·8	1·6	1·1	1·7	1·2	1·3
Capric	1·9	2·0	2·3	2·1	3·2	3·8	2·2	3·1
Lauric	3·1	3·9	4·3	3·4	7·3	6·5	4·0	4·1
Myristic	9·7	10·6	10·8	6·9	17·1	10·6	10·4	11·1
Palmitic	27·6	28·1	28·4	29·0	27·0	26·3	26·1	27·3
Stearic	12·2	8·5	9·4	7·6	4·8	8·3	6·5	11·5
Arachidic	0·7	1·0	0·5	0·9	—	1·2	—	0·6
Oleic	34·3	36·4	33·1	40·1	31·7	32·9	40·9	31·3
Linoleic	4·4	3·7	5·4	3·6	2·4	3·6	4·1	4·5

Examination into the manner in which the fatty acids are linked with glycerol was carried out by Caldwell and Hurtley (J C.S. 1909, 69, 853), who distilled *in vacuo* both the glycerides and the acids. They conclude there is no tributyrin and probably no triolein present. Amberger (Z. Nahr. Genussm. 1918, 35, 313) isolated 2 4% of triolein, but no tributyrin. Hilditch and Jones (*l c.*) conclude from their study of the component glycerides that about 30% of the glycerides contain fully saturated acids of the complex mixed type, the remainder consisting of mixed glycerides of saturated and unsaturated acids: there is probably little triolein.

The results of Hilditch and Jones confirm the conclusions of Arup (Analyst, 1928, 53, 641), who separated butter fat into various fractions by appropriate crystallisation and determined the usual constants on the fractions.

The composition of butter fat is affected by a number of factors, e g the food of the cow, particularly special foods; the period of lactation, that is, the time elapsed since calving; conditions under which the cow has been kept, such as change from summer to winter housing, and the reverse; the breed of cow; the age of the cow. A great many observations have been made and the original publications should be consulted.

Barthel and Zouden (Z Nahr. Genussm. 1914, 27, 439) show the effect of feeding with coconut cake and beetroot leaves; Cranfield and Taylor (Analyst, 1915, 40, 433) linseed cake and hempseed cake, and (*ibid.* 1916, 41, 240) dried yeast and cotton meal; Cranfield (*ibid.* 1916, 41, 336) ground nut cake and decorticated cotton cake; Eccles and Palmer (Missouri Agric Exp. Sta. Res. Bull. 1916, 27) cotton seed products, Bengtsson (Z. Nahr. Genussm. 1922, 44, 326) babassu fodder; Holland and others (J. Agric. Res. 1923, 24, 365) various fatty foods; Channon, Drummond, and Golding (Analyst, 1924, 49, 311) various oils; and Hilditch and Sleightholme (Biochem. J. 1930, 24, 1098) the effect due to changes in seasonal and feeding conditions Brownlee (Proc. Roy. Soc. Dublin, 1925, 18, 49) has demonstrated the abnormal character of Irish winter butter, and Arup (Analyst, 1929, 54, 634) gives the results of the analysis of Irish creamery butter in the winters of 1927–8 and 1928–9. Hilditch and Thompson (Biochem J. 1936, 30, 677) have investigated the effect of some ingested fatty oils upon the character of the butter glycerides; and Hilditch (Analyst, 1937, 62, 250) gives a review of the minor component acids in butter fat, and their possible significance.

Butyric acid is the constituent of the fat by which the fluctuation may be most readily ascertained. In spring and summer the proportion is highest, and ordinarily lowest in autumn and winter, due to changes in housing and food, and also to period of lactation. The accurate estimation of the absolute amount of butyric acid is a lengthy process and an empirical method has been generally adopted (*see* Examination of Butter fat).

Butter fat has $d^{37\,8}_{37\,8}$ 0 910–0 913 (Thorpe, J.C.S. 1904, 85, 249); the reading with the Zeiss butyro refractometer at 45° is usually between 38 and 42, the Koettstorfer number, or saponification value, i e. the quantity of potash expressed in mg. required to saponify 1 g. of fat, is on the average between 220 and 232 5. All these values bear a close relationship to one another, and to the Reichert number, as will be seen by the following table (Thorpe, *l.c.*) which also gives the percentages of soluble and insoluble acids, and the mean molecular weight of the latter:

No of samples	Reichert-Wollny number	Specific gravity at 37 8°	Saponification value	Zeiss at 45°.	Soluble acids, % on fat	Insoluble acids, % on fat.	Mean molecular weight of insoluble acids
7	22 5	0 9101	219 9	42 0	4·3	90 1	266 9
17	23 5	0 9104	221·3	41 5	4·5	89·7	265 5
15	24·5	0 9108	223 3	41·5	4 7	89 4	265 0
27	25 5	0 9110	223 4	41·3	4·8	89 3	264 2
37	26 5	0 9113	225 3	41 0	4·9	88 9	261 9
51	27·5	0 9114	226 7	40 6	5 2	88·7	261 7
78	28 5	0 9118	228 3	40 1	5·4	88 4	260 9
56	29 5	0·9120	229·9	40·1	5 6	88 3	259 6
41	30 5	0 9123	231·4	39·9	5·8	87·9	260 1
18	31·3	0 9125	232 2	39 7	5·7	87 9	258 0
10	32 6	0 9130	232 5	39·4	6 0	87 7	257 8
357							

The iodine value indicates the proportion of unsaturated acids, essentially oleic and linoleic, in the fat, and is closely related to the consistency of the butter. Like the values given in the above table, it is subject to seasonal variations. Kilde and Winther (Milch Forsch. 1930, 10, Heft 3, 228) found the values to vary from 29 9 for Danish winter butter to 41·4 for summer butter; and Haglund, Wode and Olsson (Bull. 387 (1930) Centralanstalten) similarly found 31 to 40 for Swedish butter Arup (Analyst, 1932, 57, 610) found rather less variation in Irish butter. Here again, the lactation period and winter feeding affect the results. It is of advantage to maintain a high iodine value, and thus reduce the firmness of

butter in the winter months, by feeding with suitable oilcakes. This matter received the special attention of the International Dairy Congress in Copenhagen in 1931.

Arup (*l.c.*) has used the thiocyanogen process described by Kaufmann (Analyst, 1926, **51**, 157) for determining the linoleic content of butter fat, and it would appear from his results that the linoleic value does not undergo the same variation as the oleic.

Dean and Hilditch (Biochem. J. 1933, **27**, 889) find that there is an abrupt increase in the proportion of unsaturated acids as indicated by the iodine value on putting cows to grass in the spring. The iodine value appears also to increase with the age of the cow.

The unsaponifiable matter of the fat has been determined by Boemer (Z. Nahr. Genussm. 1898, **2**, 81) and Kirsten (*ibid.* 1902, **5**, 833) who found from 0·31 to 0·43%. It contains cholesterol, as distinct from phytosterol, which is present in many vegetable oils.

3. **Curd.**—The total amount of curd in well-made butter is about 1%. The Government Laboratory (J. Board of Agric. 1912, **19**, 750) found in imported butter 0·4 to 1·86%, average 1·04%. In 366 samples only 11 contained more than 1·5%. Butter from factories in Great Britain ranged from 0·34 to 1·86%.

The curd consists mainly of casein. Richmond (Analyst, 1906, **31**, 178) found 0·38% average, and 0·5% maximum. Van Slyke and Hart (Amer. Chem. J. 1905, **33**, 461) state that when cream contains more than 0·5% of lactic acid—a quantity exceptionally high for churning—the casein is present as casein lactate, but in butter made from sweet cream, as calcium casein.

The amount of lactose in the curd is very small, usually less than 0·2%, since lactose is soluble in water and is largely removed by efficient washing.

The mineral matter, exclusive of added salt, is derived from the buttermilk enclosed in the butter mass, and from any salts of casein adhering to the fat, together with traces from any hard water used for washing the butter. The total amount is usually below 0·1%.

4. **Colour.**—The natural colour of butter is due to carotene, xanthophyll, and probably some other carotenoid bodies. These pigments are synthesised by plants but not by higher animals. Hence the colour of butter arises from the food of the cow. Other mammalian milk fat is mainly colourless.

Carotene is capable of conversion into vitamin A, and hence the natural colour of butter may afford a guide, although not complete, to the vitamin A content of butter.

Butter is usually artificially coloured in order to produce regularly an article of the same standard tint. Various coal tar and vegetable colours are used for this purpose, but by the Public Health Regulations (*l.c.*) certain colours are not allowed to be used.

5. **Aroma and Flavour.**—The characteristic odour of butter was at one time considered to be due to small amounts of free fatty acids and to traces of glycerides of fatty acids lower than butyric. Recent work, however, shows that the odour is connected with the presence of diacetyl. Niel, Kluyver and Derx (Biochem. Z. 1929, **210**, 234) and Schmalfuss and Barthmeyer (*ibid.* 1929, **216**, 330) found diacetyl; Davies (Food Manuf. 1933, **8**, 346) and Barnicoat (Analyst, 1935, **60**, 653) give methods for its detection and determination.

Davies (*l.c.*) suggests that acetyl methyl carbinol, a metabolic product of many types of micro-organisms, arises in the ripening of cream, and that this is oxidised by air and free oleic acid during churning and the early stages of storage, to diacetyl. In some cases, however, the oxidation may proceed too far, and may be connected with the causes which lead to butter from ripened cream having inferior keeping qualities compared with butter from sweet cream.

Synthetic diacetyl is a greenish-yellow liquid with the characteristic butter odour, and incorporated into flavourless butter in very minute proportions is capable of imparting butter flavour and odour.

The Chief Medical Officer of the Ministry of Health (Annual Report, 1932) states that the best dairy butter may contain about 0·0005% of diacetyl, to which the aroma is due, and that a solution of synthetic diacetyl is used to impart aroma to butter deficient in this quality. He also points out that since diacetyl has definite oxidising action on fats, it may have destructive action on vitamin A.

Wildman (J. Assoc. Off. Agric. Chem. 1937, **20**, 93) describes a method for the determination of mould in butter.

Vitamins in Butter.

Butter fat is a valuable source of vitamins A and D; and the literature on investigations into the causes which influence their content and variation in butter is extensive and constantly increasing. The total vitamin A value of a butter is derived from vitamin A already existing in the butter and carotene which is converted in the body into vitamin A; but there is no constant relation between the two sources, and owing to the general use of artificial colouring any guide that the natural colour might afford as to the amount of vitamin A is lost.

Both vitamin A and carotene readily undergo changes on oxidation, so that the physiological value of butter may be seriously impaired if the cream, before churning, or the butter is subjected to any treatment involving action of air or other substance conducive to oxidising action, such as removing bad odour or rancidity by blowing air through cream or melted butter fat as in butter renovation (*see* Drummond and others, Biochem. J. 1921, **15**, 540).

The vitamin A content is influenced by climatic and housing conditions, and especially by feeding. Booth and others (Biochem. J. 1933, **27**, 1189) state that the total vitamin A activity of summer butter from Shorthorn cows appears to be three times greater than that of winter butter, and that the fraction of total activity due to carotene is greater in summer. Gillam and others (Biochem. J. 1933, **27**, 878) show that butter from cows fed on normal winter rations—hay and concentrates—falls in colour

and vitamin A values and remains at a low level till cows go to pasturage, when there is a rapid rise. If, however, the cows are fed on artificially dried grass, the colour and vitamin A contents increase rapidly, more especially when the grass during growth has been treated with nitrogen fertiliser. They found ordinary grass silage to be little superior to hay.

Watson and others (Biochem. J. 1934, 28, 1076) found a large increase in both values on adding to dried grass a special fodder prepared on the ensilage plan by treating grass with dilute mineral acid, and storing without access of air.

Booth, Kon and Gillam (Biochem. J. 1934, 28, 2169) found that there was no difference in vitamin A activity of the butters obtained from the two breeds of cows, Shorthorn and Guernsey, kept through three seasons under similar conditions. The relative contributions of carotene and pre-formed vitamin A varied considerably, although the total of the two might be the same. They also compare the growth-producing activity of vitamin A with that of carotene. Baumann and others (J Biol. Chem 1934, 105, 167) also record the effects of breed and diet on vitamin A and carotene content of butter. Coward and Morgan (Brit. Med. J 1935, 1041) give the values in international units for vitamins A and D in butter; and Morgan and Pritchard (Analyst, 1937, 62, 354) record the average vitamins A and D potency of butter. Gillam and others (Biochem J. 1936, 30, 1728) give a series of results of the determination of vitamin A and carotene contents of butter fat from cows of various breeds covering summer and winter periods with regard to diet and stage of lactation.

The influence of maize, cottonseed meal, pasturage and silage in varying conditions of feeding has also been recorded by Fraps and Treichler (Ind. Eng. Chem. 1933, 24, 1079) Baumann and Steenbock (J. Biol Chem. 1933, 101, 547) state that there is no loss of either vitamin A or carotene from storage of butter for six months at 0°.

Butter fat also contains the anti rachitic vitamin D, which is formed from ergosterol when foodstuffs containing it are exposed to sunlight. Drummond (Roy. Soc. Arts, Cantor Lectures, 1932, 19) states that pasture, eaten while fresh from exposure to the sun's rays, may supply vitamin D, and "to some extent this explains the rise in the calcifying value of milk which occurs when cows are out on pasture in summer." Gillam and others (*l.c.*) record the presence of ergosterol in the unsaponifiable matter of grass. Kon and Booth (Biochem. J. 1933, 27, 1302) suggest that there is a chemical difference between the anti-rachitic factor of butter and those of cod liver oil and irradiated ergosterol.

Butter fat also contains a small quantity of vitamin E (Drummond, *l c.*).

Analysis of Butter.

The analysis of butter comprises: (1) the determination of the amounts of water, fat, curd and salt; (2) the examination of the fat to ascertain whether it is milk-fat only; and (3) special tests for the presence of preservatives, prohibited colouring matters and other substances foreign to butter.

The ordinary examination does not at present include a determination of vitamin activity. For this, if required, references are given below.

Preparation of Sample.—A quantity of not less than 50 g. is placed in a bottle with wide mouth, and the bottle is closed securely with screw cap or glass stopper. It is then heated at a temperature of about 50° until the butter fat has melted, when it is vigorously shaken to emulsify thoroughly the fat and water. The shaking is continued during cooling, until the butter has practically set.

Water.—From 5 to 6 g. of the prepared sample are weighed into a flat-bottomed dish containing a glass rod with flattened end. The dish is heated on a steam-bath for an hour with frequent stirring of the butter, after which it is cooled and weighed. The heating is repeated until the weight is constant. The operation may be greatly accelerated where many tests have to be made by using aluminium dishes heated on an aluminium plate adjusted to a temperature of 100° to 105°.

Fat.—The water-free residue in the dish is then extracted repeatedly with ether, the ethereal solution filtered through a dried and weighed filter paper, and both dish and paper washed with ether until free from fat. The residue on the paper and in the dish is the curd and salt in the quantity of butter taken.

The weight of fat may be found by difference, or it may be ascertained directly. In this case, the ethereal solution is filtered into a small flask, the ether distilled off, and the residue in the flask dried to constant weight.

Curd and Salt.—In the case of butter free from salt, the curd is the residue not soluble in ether contained on the paper and in the dish after the foregoing operation. It may also contain all or some portion of the preservative if such is found to be present.

In the case of salt butter, the dish and paper after weighing are extracted with hot water, and the solution titrated with standard silver nitrate solution to obtain the weight of common salt.

In some cases of high curd it may be necessary to ascertain by direct estimation of the proteins and lactose whether milk products, such as dried skim milk, have been added. For this purpose a larger quantity of butter, about 50 g., should be taken, dried, and extracted with ether; and the residue used for the determination either of protein by the Kjeldahl process or of lactose by Fehling's solution. If both determinations are to be made, the residue is washed into a beaker with water, acidified with acetic acid, and the protein precipitated by careful addition of Fehling's copper sulphate solution. This precipitate is filtered on a weighed paper, dried, and weighed and ashed Its weight after deducting the ash = the protein. The filtrate is made up to 100 ml., and an aliquot portion taken for lactose determination.

Examination of Butter fat.—The emulsified butter remaining in the bottle after removal of the quantity for determination of water and curd, is again melted, the water allowed to settle, and the clear fat poured through a dry

paper, to obtain fat for examination as to purity.

The distinctive feature of the glycerides of butter fat is the presence of a considerable proportion of butyric acid, which is volatile and soluble in water. In this respect butter fat differs from most other known edible oils and fats. It also contains a small quantity of the next higher homologues of butyric acid: these also are volatile but much less soluble in water. A few vegetable oils such as coconut and palm kernel also contain some of these volatile, insoluble acids, but the main body of edible oils and fats, both animal and vegetable, and hydrogenated fats, capable of use as adulterants of butter, such as refined lard, beef fat, hardened oils, have practically no volatile acids. Hence the addition to butter fat of this latter class of fats simply reduces the proportion of volatile acids in the mixture, but the addition of the coconut and palm kernel class, while reducing the volatile soluble acids, increases the volatile insoluble acids.

The method employed for determining the proportion of volatile soluble acids was first suggested by Reichert (Z. anal. Chem. 1879, **18**, 68), modified by Meissl (J.C.S. 1880, A, 828), and by Wollny (*ibid.* 1888, A, 200); and is now variously known as the Reichert-Meissl or Reichert-Wollny process. It was adopted by a Committee, consisting of the Government Chemist and the Society of Public Analysts, for ascertaining the amount of butter fat in margarine (Analyst, 1900, **25**, 39), and is now used with some modifications for the examination of butter fat for purity. To it has been added the Polenske process (Z. Nahr. Genussm. 1904, **26**, 273) by which a value of the insoluble volatile acids is obtained.

In an inquiry carried out by the Committee on Butter Regulations it was shown that the figure for normal butter by this empirical method fell between 24 and 32, and the Committee recommended a presumptive minimum standard of 24 (Report, Cd. 1749, 18). This figure has, however, not been adopted by regulation. While a low Reichert number may be obtained from genuine butter in certain circumstances, a similar result may also be obtained from a mixture of butter, with a naturally high number, and other fat free from butyric acid. To meet this natural variation in genuine butter, and to prove in suspected cases that the butter though having a low Reichert number is genuine, the Netherlands Government has instituted a system of butter control, under which the associated creameries are under inspection, and the Reichert numbers of the butter produced therein regularly ascertained. Consignments from the creameries bear distinctive labels, so that the Reichert number of a sample taken in commerce can be compared with those of the butter produced in the factory of origin.

It is essential in using the method that the exact conditions should be carried out in every detail; otherwise the results obtained by various workers are not comparable. Revis and Bolton (Analyst, 1911, **36**, 335) give the method as follows:

5 g. of fat and 20 g. of glycerol are weighed into a 300 ml. flask, and 2 ml. of 50% $NaOH$ solution added. The flask is heated over a flame with constant shaking until the contents clear suddenly; the soap is then cooled, 100 ml. of recently boiled-out water added, and the soap dissolved; 0·1 g. of powdered pumice sieved through butter muslin is added, and then 40 ml. of sulphuric acid solution (20 to 25 ml. of strong H_2SO_4 diluted to 1,000 ml. and the solution adjusted so that 35 ml. neutralise 2 ml. of $NaOH$ solution). The flask is at once connected with the condenser and heated with a small flame until the insoluble acids are completely melted; the flame is then increased and 110 ml. distilled in 19 to 21 minutes. The temperature of the condenser water should be from 18° to 20°C. and the dimensions of the apparatus are to be the same as given by Polenske. When 110 ml. have distilled, the flame is removed, and a 25 ml. cylinder is placed under the condenser to catch any drops. The 110 ml. flask and contents are stood in water at 10° to 15°C. for 15 minutes. After mixing, the contents of the 110 ml. flask are filtered and 100 ml. titrated with $\frac{N}{10}$ baryta, using 0·5 ml. of a 1% solution of phenolphthalein as indicator. The number of ml. required for neutralisation increased by one-tenth after subtraction of the blank (which must be determined in an exactly similar way, by using all the reagents except the fat) is the *Reichert-Meissl value.* The condenser, cylinder, and 110 ml. receiver are washed with 18 ml. of cold water, which are then poured onto the filter already used and the filtrate rejected. The condenser is then washed out with four successive portions of 10 ml. of neutral alcohol, which are received in the cylinder and poured over the filter into the 110 ml. flask, the mixed alcohol solutions being then titrated with $\frac{N}{10}$ baryta, using phenolphthalein as indicator. A blank value is obtained in a similar way. The number of ml. of $\frac{N}{10}$ baryta used, less the number used for the blank, is the *Polenske value.*

Revis and Bolton (*l.c.*) put forward the following table as a guide to the relationship between the Reichert-Meissl and Polenske values in genuine butter.

Reichert-Meissl values.	Polenske values.
32	3·5
31	3·2
30	3·0
29	2·9
28	2·7
27	2·4
26	2·0
25	1·8
24	1·7
23	1·6

It must, however, be understood that many other results have been obtained by various observers, and should be examined before con-

demning a butter which does not conform to these limits.

Richmond and Hall (J S C.I. 1920, 39, 80T) point out that the time of distillation should be strictly adhered to, and Bolton, Richmond and Revis (Analyst, 1912, 37, 185) draw attention to the position of the hole in the still head. The size and quantity of the pumice is also important. Kirkham has studied the effect of atmospheric pressure during distillation (Analyst, 1920, 45, 293). Cocks and Nightingale (*ibid* 1928, 53, 322) show the need of precautions to be taken to prevent sulphuric acid entering the distillate.

Another useful value which may be obtained in connection with the above is that due to Kirschner (Z. Nahr. Genussm. 1905, 10, 265). This is based on the solubility of silver butyrate, the silver salts of the higher homologues being practically insoluble. Revis and Bolton (*l.c.*) proceed as follows:

To the 100 ml. of the 100 ml. distilled and titrated with baryta (care having been taken not to exceed the neutral point) is added 0 5 g. of finely powdered silver sulphate, and the whole allowed to stand for an hour with occasional shaking. The liquid is then filtered, 100 ml. measured off, 35 ml. of water, and 10 ml. of sulphuric acid (as previously employed) added, together with a long piece of aluminium wire, and 110 ml. again distilled off in the standard Reichert-Polenske apparatus in 20 minutes; 100 ml. are titrated, and the number of ml. so obtained, corrected for the blank, is calculated to the Kirschner value by the following formula:

$$K. = X \times \frac{121 \times (100+Y)}{10,000}$$

where X = the corrected Kirschner titration;
Y = the number of ml of baryta used to neutralise 100 ml. of the R. M. distillate.

Since the Kirschner value is practically that of butyric acid, after removal from the Reichert-Meissl value of the partly soluble higher homologues, it is lower compared with the corresponding Polenske value than the original Reichert-Meissl value. Thus butters with a range of 1·6 to 3 2 Polenske values would have Kirschner values of 20 to 26, and Reichert-Meissl values of 23 to 32. Cranfield (Analyst, 1915, 40, 440) gives the Reichert, Kirschner and Polenske values for a number of individual butters. A number of determinations have been made of the effect upon the Reichert, Kirschner and Polenske numbers by admixture of butter with various proportions of coconut oil and palm kernel oil (*see* Elsdon and Smith, Analyst, 1925, 50, 53; *ibid.* 1926, 51, 73; Revis and Bolton, *l.c.*; Bolton, Richmond and Revis, Analyst, 1912, 37, 183).

Other analytical methods used in the examination of butter fat are those of Shrewsbury and Knapp (Analyst, 1910, 35, 385); Caldwell and Hurtley (*ibid.* 1909, 34, 274); Fendler (Z. Nahr. Genussm. 1910, 19, 544); and Avé Lallemant (*ibid.* 1907, 14, 317). This last method, which depends upon the respective solubilities of the barium salts of the fatty acids, has received some attention, particularly in the examination of ghee (*see* Bolton and Revis—Allen's "Commercial Organic Analysis," 5th ed, 1924, vol. II, p. 381).

Bhchfeldt (J.S.C.I. 1919, 38, 150T) has introduced a modified Kirschner process, and this again has been modified by Gilmour (Analyst, 1920, 45, 2).

The foregoing tests are based upon the disturbance by adulterants of the ratio existing in normal butter between soluble and insoluble acids, and volatile and non-volatile acids If this ratio is abnormal, other values are also affected, for example, the saponification and iodine values, the Zeiss number, and the specific gravity These regular constants must, therefore, be determined by the usual methods of fat analysis and the results carefully studied. The question of the influence of feeding, housing, climatic conditions, period of lactation, must also be considered.

Additional physical methods which may be of value are the Valenta test and the Crismer test.

Valenta Test.—3 c.c. of fat are dissolved by warming in an equal volume of glacial acetic acid, and then allowed to cool while being stirred with a thermometer. Immediately a turbidity is noticed, the temperature is read. A modification introduced by Jean is to measure the volume of acid dissolved in the fat at 50°. (For recent investigation of factors affecting the Valenta test, *see* Fryer and Weston, Analyst, 1918, 43, 3.)

Crismer Test.—0 5 c.c. of melted fat and 1 c.c of absolute alcohol are placed in a tube fitted with cork and thermometer, the bulb of which dips into the liquid. The tube is gently heated inside a larger tube until the liquid becomes homogeneous. It is then allowed to cool, and the temperature noted when turbidity appears. This point is the critical temperature of dissolution (Crismer, Analyst, 1897, 22, 71) Vandam has shown how the alcohol used in the test may be standardised by means of petroleum spirit (Ann. Falsif. 1919, 260).

In some cases it may be possible to obtain direct evidence of the presence of fat foreign to butter by the application of specific tests If, however, the test is negative, it may not be conclusive evidence of the absence of a particular oil or class of oils. Certain specific tests depend upon the presence in the oil of a body associated naturally with it, but which may have been removed by the purification necessary to make the oil suitable for admixture with butter In the case of a positive result, confirmation must be obtained from other tests, such as the chemical and physical constants, since particular feeding may have caused the reacting substance to pass into the milk.

1. *The Phytosterol Test for the Presence of Vegetable Oil.*—The original test of Bömer (Z. Nahr. Genussm. 1901, 4, 1070) has been much improved by the use of digitonin as precipitating agent (*see* Steuart, Analyst, 1923, 48, 155, and More, *ibid.* 1929, 54, 735). More's method is as follows:

Saponify, using reflux condenser, 15 g. of filtered fat with 9 5 ml. of KOH solution (1,000 g. of KOH in 1,400 ml. of water) and 20 ml. of alcohol (96%) in a 300 ml. conical

flask. Shake while warm until the fat is dissolved, and heat further for half an hour. Cool, add 60 ml. of water and 180 ml. of alcohol (96%), mix, and add 10 to 20 ml. of digitonin solution (1% of Merck's digitonin in 96% alcohol). Allow the mixture to stand for 24 hours in a cool place and filter on Buchner funnel with a closely fitting paper. Wash with a small amount of alcohol to remove soap. The digitonin-sterol compound flakes off on drying. Weigh the steride and acetylate it with ten times its weight of acetic anhydride.

The mixed acetates obtained as above, or by Bömer's original process, are dissolved in alcohol, the solution evaporated carefully, the acetates crystallised, and the m.p. of the separated crystals taken. The crystallisation is repeated several times, and the m.p. taken each time.

The test depends upon the difference in m.p. of the cholesteryl acetate obtained from butter and other animal fats, and the phytosteryl and allied steryl acetates from vegetable oils. The former melts at 113·5° to 114·5°; the latter melt at some point above 125°. If the butter is pure the m.p. should not exceed 115°; slight increases above 115° may arise from feeding on coconut cake, but if the m.p. is above 116°, added vegetable fat is indicated, and should be reflected in the numbers for the analytical constants.

2. *Hinks's Test for Coconut Fat* (Analyst, 1907, 32, 160).—5 ml. of butter fat are dissolved in 10 ml. of ether in a tube, and the tube packed in ice for half an hour. The solution is then rapidly filtered, the ether evaporated from the filtrate and the residual fat dissolved in 96% alcohol. The solution is gradually cooled, and then maintained at 5° for 15 minutes, when it is rapidly filtered, and the filtrate cooled to 0°. The deposit separating at this temperature is examined on a cold microscopic slide under a power of from 250 to 300. Butter fat yields a deposit of round granular masses; coconut fat, fine needle-shaped crystals, and mixtures of butter and coconut fat, fine feathery crystals attached to the granular butter masses. The test is capable of detecting 5% of coconut fat in butter, but the presence of other fat—notably lard—interferes somewhat with the test.

3. *Badouin Test for Sesamé Oil.*—5 ml. of butter fat are mixed in a tube with 5 ml. of HCl (sp.gr. 1·19) and 0·1 ml. of a 2% furfural solution. The mixture is well-shaken and allowed to stand. In presence of sesamé oil the aqueous layer which separates is of a reddish colour. Butter coloured with certain aniline dyes gives a pink to violet coloration with hydrochloric acid, and in such a case the acid and fat mixture must be heated until colourless before addition of furfural.

4. *Halphen Test for Cotton-seed Oil.*—5 ml. of butter fat are dissolved in 5 ml. of amyl alcohol, 1 ml. of a solution of sulphur in carbon disulphide is added, and the mixture heated for 20 minutes at 105° in a brine bath. A red coloration is produced in presence of cotton-seed oil.

The substances giving rise to the reactions in both Badouin and Halphen tests are affected by processes of oil purification or by hydrogenation. Furthermore, a positive reaction may arise from feeding with cake containing sesamé or cotton-seed oil.

Colouring Matters.—It is unlikely that metallic colouring bodies will be present. If suspected the usual tests for metals must be applied.

The prohibited organic colours are gamboge, and the five coal tar dyes already cited (p. 159). Nicholls (Analyst, 1927, 52, 585, and *ibid.* 1929, 54, 335) points out that all these colours are of an acidic character, and may be removed from methylated ether solution, or in the case of aurantia from a mixed light petroleum and methylated ether solution, by means of alkali. For this purpose make an ammoniacal extract by shaking an ethereal solution of the fat with water and dilute ammonia. To the ammoniacal extract add one drop of methyl orange, neutralise with acid, then make acid to about $N/100$ to $N/50$. Extract the acid solution with methylated ether, transferring the ether to a separating funnel. Extract this with successive quantities of 5 to 10 ml. of approximately $N/100$ sodium hydroxide. Then add an equal quantity of light petroleum to the methylated ether and again extract with dilute caustic soda.

If there is no colour in the alkaline extract, all the prohibited dyes are absent. In presence of a colour the scheme of Nicholls (*l.c.*) should be followed.

If it is desired to ascertain what vegetable or other organic dye has been employed for colouring butter, the scheme given by Bolton and Revis (Allen's "Commercial Organic Analysis," 5th ed., vol. II, 1924, 405) may be followed.

Examination for Preservatives.—The use of preservatives, other than common salt, in butter is prohibited in this country. The tests given below relate to preservatives formerly employed, but there is also a possibility of the use of other substances not in the list.

1. Place 5 or 10 g. of butter in a separating funnel, add sufficient chloroform to take the fat into solution, and then 25 ml. of water rendered slightly alkaline with $N/10$ soda, and shake gently. Allow to settle. The aqueous extract may be used for the following qualitative tests:

(*a*) *Boric Acid.*—Run 1 ml. of the extract into a porcelain dish, add a drop of hydrochloric acid, and 10 drops of turmeric solution. Evaporate to dryness. In the presence of 0·02% of boric acid a purple-red colour develops, changed to indigo by a drop of strong ammonia. For quantitative determination of boric acid, *see* Bolton and Revis (Allen's "Commercial Organic Analysis," 5th ed., vol. II, p. 409).

(*b*) *β-Naphthol.*—To a little of the extract add an emulsion of diazotised naphthionic acid, β-naphthol gives *immediately* a crimson colour.

(*c*) *Cinnamic Acid.*—Oxidise a few ml. of the extract with chromic acid. On cooling there is an odour of benzaldehyde if cinnamic acid were present.

(*d*) *Fluoride.*—Evaporate 10 ml. of the extract in a platinum crucible, incinerate the residue, and heat with strong sulphuric acid, covering the crucible with a watch-glass coated with wax through which a design has been scratched. In presence of fluoride the glass will be etched.

2. *Benzoic and Salicylic Acids.*—Mix 10 g. of butter with alcohol acidified with sulphuric acid, and heat at b p. for half an hour. Cool and transfer the alcoholic solution to a separator. Dilute with water and extract with ether. Then extract the ethereal solution with dilute ammonia.

(*a*) Render just acid a few ml. of the extract and add a drop of ferric chloride solution. A violet coloration indicates salicylic acid.

(*b*) Evaporate a portion of the extract to dryness in a porcelain dish, just acidify with acetic acid, and add a drop of ferric chloride solution. Benzoic acid gives a buff coloured precipitate. For the estimation of benzoic and salicylic acid, *see* Nicholls, Analyst, 1928, 53, 19 Illing (*ibid* 1932, 57, 224) gives Mohler's test for benzoic acid, as applied both qualitatively and quantitatively.

The determination of benzoic acid in foods is dealt with by Monier-Williams (Min. of Health Report No 39)

Determination of Vitamins.—The recorded results have been mainly obtained by biological experiments. Wokes and Willmott (Biochem. J 1927, 21, 419) and Drummond and Hilditch (Empire Marketing Board, Report 35, 1930) put forward a chemical-colorimetric test for vitamin A, but this can only be applied with colourless butter, since carotenoids give the same reaction Heilbron and Morton (Biochem. J. 1930, 24, 870) suggest a spectrographic method for both vitamin A and carotene.

Ferguson and Bishop (Analyst, 1936, 61, 517) describe a method for estimation of carotene in butter.

The vitamin D content of a substance is estimated by comparison with that of a particular preparation of irradiated engosterol, issued by the National Institute for Medical Research, as a standard of reference.

General.—Stokoe (J S.C I. 1921, 40, 75T) has investigated the production of rancidity in butter. Browne (Ind. Eng. Chem. 1925, 17, 44) gives results of examination of butters kept for lengthy periods; Elsdon, Taylor, and Smith (Analyst, 1931, 56, 515) and Arup (*ibid.* 1929, 54, 736) give the Reichert, Kirschner and Polenske values of rancid butters. Rogers and associates ("Fundamentals of Dairy Science," Reinhold Publishing Corpn. 1935) point out the influence of small quantities of metals, and the lipolytic action of carelessly made starters.

Minster (Analyst, 1932, 57, 615) has investigated the keeping qualities of unsalted butter.

Kreis' reaction as carried out by Kerr (Ind. Eng. Chem. 1918, 10, 471) is a chemical means for comparing rancidities. Waters and Zurn (Z. Unters. Lebensm. 1935, 70, 353; 1936, 72, 140) use the peroxidase reaction as a means of testing whether butter has been made from pasteurised or unpasteurised cream.

The National Physical Laboratory (Report, 1931) has investigated the effects produced by working butter, and by prolonged storage, at temperatures below and near freezing-point, and also the relative spreadability of butter. Arup (Analyst, 1932, 57, 300) gives results of examination of samples of bog butter (*q v*) recently discovered, and information relating to the practice of preserving or storing butter by burying it.

BUTTER FAT FROM MILK OF OTHER MAMMALS.

(*a*) *From Prepared Butter.*—The butters prepared from the milk of goats and sheep by the ordinary churning process has been examined and the results given by Knowles and Urquhart (Analyst, 1924, 49, 509) and Stathopoulo (J. Pharm. Chim. 1933, 125, 287). The latter states that the butters were very rich in vitamin A.

(*b*) *From Ghee (Indian) or Samna (Egyptian)*.—The method of preparation of these fats may affect their composition especially as regards the proportion of volatile acids. The milk is churned by shaking in skins (Egypt) or beating with split bamboos (India). In Egypt the separated butter fat or "zibda" is collected from the small producers in the villages by the samna makers, and heated in large pans to get the clear, melted fat which is marketed as "samna" In India the butter fat, collected from the churning, is heated at once, when a clear, melted fat in sweet condition is obtained, or, as is frequently the case, it is allowed to stand until somewhat rancid before being heated.

Bhattacharya and Hilditch (Analyst, 1931, 56, 161) have investigated the composition of the glycerides of buffalo ghee and cow ghee. Other results of ghee and samna of various origin—buffalo, sheep, goat—are recorded by Atkinson (Analyst, 1928, 53, 520), Trimen (*ibid.* 1913, 38, 242), Ghose (*ibid.* 1920, 45, 444), and Bolton and Revis (Allen's "Commercial Organic Analysis," 5th ed., 1924, vol. II, 431). G. S.

BUTTER, MINERAL. A term formerly applied to several of the metallic chlorides, *e g* chlorides of antimony, tin, bismuth, zinc, etc.

BUTTER NUTS *v.* BUTTER, VEGETABLE.

BUTTER, VEGETABLE. A term applied to any greasy fat of vegetable origin which possesses a consistency resembling that of butter or lard. "Shea butter" (from *Butyrospermum Parkii*), "illipé butter" (from *Bassia longifolia* L, *cf.* Bassia Fats), "nutmeg butter" (from nutmegs) may be cited among the industrial fats, whilst the *edible* vegetable butters (frequently termed "nut butters") include shea butter, cacao butter, refined coconut and palm kernel oils, etc. The "butter- or tallow-tree" of Sierra Leone is *Pentadesma butyracea* Sabine, from the seeds of which "kanya butter" is obtained. *Bassia butyracea* Roxb. is occasionally known as the "Indian butter tree" (*see Phulwara Butter*, BASSIA FATS). Seeds imported into Europe from Brazil under the name of "butter nuts" are derived from *Caryocar tomentosum* Willd. (*C. butyrosum* Willd.) and are the source of the fat known as "souari-" or "sawarri fat." E. L

BUTTGENBACHITE. A rare nitrate mineral,

$$2CuCl_2\cdot Cu(NO_3)_2\cdot 15Cu(OH)_2, 4H_2O,$$

forming a felt of sky blue hexagonal needles resembling connellite,

$$2CuCl_2\cdot CuSO_4\cdot 19Cu(OH)_2,$$

with which it is isomorphous. It occurs with

copper ores in Katanga, Belgian Congo (A. Schoep, Compt. rend. 1925, 181, 421; H. Buttgenbach, Ann. Soc. Géol. Belg. 1926, 50, Bull. 35). L. J. S.

BUTTON LAC. Shellac melted under boiling water and solidified in round flat pieces.

-BUTYL, C_4H_9.—There are four isomeric univalent radicals of this name and formula, as shown in the following mono-derivatives:

(1) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X$, normal, (*n*-).
(2) $CH_3{\cdot}CH_2{\cdot}CHX{\cdot}CH_3$, secondary, (*sec*-).
(3) $(CH_3)_2CH{\cdot}CH_2X$ (*iso*).
(4) $(CH_3)_3CX$, tertiary, (*tert*-).

Butyl Compounds.

Butyl Alcohols, $C_4H_9{\cdot}OH$.—All the four isomers are known.

Various general methods have been described for the purification of the alcohols obtained in the crude state. Among these are the separation with high-boiling mineral oil followed by fractionation of the non-aqueous layer (Canad. P. 257750). Orton and Jones (J.C.S. 1919, 115, 1194) describe a method for purifying *n*-butyl alcohol using the sodium salt of the salicylate.

Verley (Bull. Soc. chim. 1928, [iv], 43, 469) has suggested a method of quantitative determination by acetylation with acetic anhydride and acetyl chloride in the presence of pyridine. The water content of commercial butanols may readily be determined by the method of Spiers (J.S.C.I. 1924, 43, 251T) by distillation with a known excess of benzene and weighing the fraction collected up to 100°. Hannotte (Bull. Soc. chim. Belg. 1926, 35, 86) has studied the characteristics of various azeotropic mixtures of the alcohols and esters.

Colour reactions of the various isomerides have been investigated by Ekkert (Pharm. Zentr. 1928, 69, 289) using furfural in the presence of sulphuric acid and by Weber and Koch (Chem.-Ztg. 1933, 57, 73) using the Beckmann mixture. The p-*nitrobenzoates* have been examined by Henstock (J.C.S. 1933, 216) and appear to be suitable for purposes of identification.

Refractometric and other data are recorded by Brunel, Crenshaw, and Tobin (J. Amer. Chem. Soc. 1921, 43, 561) and by Munch (*ibid.* 1926, 48, 994).

The oxidation of the alcohols at elevated temperatures in the presence of various catalysts has been investigated by Rubinstein and others (J. Appl. Chem. Russia, 1933, 6, 278) and also by Simington and Adkins (J. Amer. Chem. Soc. 1928, 50, 1449).

1. *Normal butyl alcohol*: *butanol; propyl carbinol*, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$; b.p. 117·42° (corr.) (Thorpe and Rodger, Phil. Trans. 1894, 185, ii, 536); 117·71° (Brunel, Crenshaw, and Tobin, J. Amer. Chem. Soc. 1921, 43, 561); sp.gr. 0°=0·8233, 20°=0·8109, 40°=0·7994 98·7°=0·7738 (Lieben and Rossi, Annalen, 1871, 158, 154); 20°/4°=0·8099; n_D=1·39909 (Brühl, *ibid.* 1880, 203, 16). Has been found in the heavy oil of a faulty brandy to the extent of 49%. Is not formed in the fermentation of sugar produced by elliptical yeast (Claudon and Morin, J.C.S. 1887, 52, 714). Is produced by the action of sodium amalgam upon butyryl chloride and butyric acid (Saytzeff, Z. Chem. 1870, 108; Linnemann, Annalen, 1872, 161, 178). Also by the fermentation of glycerol by *Bacillus butylicus* and certain other bacteria in a suitable medium, the yield amounts to 9% of the glycerol used. Butyric acid and a little ethyl alcohol are also formed (Fitz, Ber. 1876, 9, 1348; Vigna, Ber. 1883, 16, 1438). Is also produced by the action of nascent hydrogen (iron and acetic acid) upon crotonaldehyde and trichlorobutaldehyde (Lieben and Zeisel, Monatsh. 1880, 1, 825, 842), and by the catalytic hydrogenation of crotonaldehyde (B.P. 147118).

Commercial production of *n*-butyl alcohol and acetone by a bacterial fermentation of potato starch was first carried out by Strange and Graham working Fernbach's process at Rainham and King's Lynn in 1913. Weizmann's process (B.P. 4845) in which maize starch was fermented by a different bacillus was substituted for the first process in 1916 and subsequently developed on a large scale by the Commercial Solvents Corporation of Maryland, U.S.A. From 1919 onwards, success depended on the sale of *n*-butyl alcohol for conversion into its acetate used in nitrocellulose lacquers, so called *cellulose finishes*, for motor cars. The American manufacture is described by Gabriel (Ind. Eng. Chem. 1928, 20, 1063) and by Gabriel and Crawford (*ibid.* 1930, 22, 1163). Fermenters holding 42,000 gallons of maize starch paste are inoculated with about 800 gallons of bacterial culture and fermented at 36° for 2 to 3 days. The liquid products, *n*-butyl alcohol, acetone, and ethyl alcohol, are recovered in the proportion of 6:3:1. A commercial quality of *n*-butyl alcohol used in nitro-cellulose solutions is defined by B.S.S. 308/1933.

Werkman and Osburn (J. Bact. 1931, 21, 20) have suggested the following method of determining the proportion of alcohols present in the fermentation mixture. The aldehydic and ketonic constituents of the mixture are precipitated as their 2:4-dinitrophenylhydrazones. The alcohols are distilled from the mixture and oxidised by a chromic-phosphoric acid mixture. The acids may then be either titrated or determined by partition using *iso*propyl ether. The same authors give an alternative method (Analyst, 1934, 59, 319) in which the acetone is determined iodometrically and the alcohols determined according to tables which are given.

Properties.—Colourless liquid, soluble in 12 parts of water, from which solution it can be separated by means of calcium chloride. Soluble in concentrated hydrochloric acid; is readily oxidised to butyric acid. Fused zinc chloride abstracts water, and yields β-butylene and smaller amounts of normal butylene (Le Bel and Greene, Amer. Chem. J. 1880–1881, 2, 24).

Bromine acting on *n*-butyl alcohol yields, with some difficulty, mono-brombutaldehyde, b.p. 235° (Étard, Compt. rend. 1892, 114, 753). The action of aluminium amalgam on the butyl alcohols, producing aluminium alkoxides, has been studied by Tistshenko (J.C.S. 1899, 76, i, 408; 1900, 78, i. 269).

Chlorination of *n* butyl alcohol in diffuse daylight at higher temperatures gives a mixture including some 60–70% of dichlorbutaldehyde-dibutyl acetal, b.p. 138°–140°/13 mm. At lower temperatures the mono chloro derivative predominates (Gault and Guillemet, Compt. rend 1922, **175**, 367, Bull Soc chim. 1923, **33**, 1792).

The following *esters* of *n* butyl alcohol have been prepared: *phosphite* (alcohol+phosphorus trichloride), b p. 122°–123°/12 mm (Milobedzki and Sachnowski, Chemik Polski, 1917, **15**, 34); *hypochlorite* (Chattaway and Backeberg, J C S 1923, **123**, 2999); *titanate* (alcohol+titanium tetrachloride), b p. 185°–187°/16 mm. (Bischoff and Adkins, J. Amer. Chem. Soc. 1924, **46**, 256); *borate*, b p 190°/220 mm. (U S P. 1668797) and *silicate* (alcohol+silicon tetrachloride), b p 160°–165°/20 mm. (Dearing and Reid, J. Amer. Chem Soc. 1928, **50**, 3058) The p-*nitrobenzyl-phthalate*, m.p. 62°, may be used for purposes of identification (Reid, J. Amer Chem Soc. 1917, **39**, 1249); *phthalate*, b p 325°, from butyl alcohol and phthalic anhydride in the presence of sulphuric acid (U.S P. 1864893). For the technically important n-*butyl acetate*, *see* Vol. I, p. 56, and B.S S 551/1934.

2. iso *Butyl alcohol*, iso*propyl carbinol*, *a-hydroxyβ- methylpropane*,

$$(CH_3)_2CH\ CH_2\ OH,$$

b p. 108 4° (Linnemann, Annalen, 1891, **160**, 238), 107·5° at 756 mm., Michael and Zeidler (Annalen, 1912, **393**, 81), 107 6° (corr.), Thorpe and Rodger (Phil. Trans. 1894, **185**, A, 538); 107·9° (Brunel *et al.*, *l c.*); sp gr. 0·7265 at 106 6°/4° (Schiff, Annalen, 1883, **220**, 102), 0 8168 at 0° (L.), 0 8069 at 15°/15°, 0 8008 at 25°/25° (Perkin, J.C.S. 1884, **45**, 468); sp. heat=0·686; molecular rotation=4 936 at 17 7° (Perkin, *l.c.*); $n_D^{17\,5}$ 1 13968 (Landolt and Jahn, Z. physikal. Chem. 1892, **10**, 317). Sp gr. of aqueous solutions (Duclaux, Ann. Chim. Phys. 1878, [v], **13**, 91):

Percentage of alcohol (by vol.)	2 5	5	6	10
Sp gr. of aqueous solution at 15°	0 9950	0 9930	0 9915	0·9875

Occurs in fusel oil from potatoes and beet (Wurtz, Ann. Chim. Phys. 1854, [iii], **42**, 129), and combined with angelic and *iso*butyric acids in Roman oil of chamomile (Fittig and Köbig, Annalen, 1879, **195**, 96).

Preparation.—By the action of sodium amalgam and water upon β-chloro*iso*butyl alcohol, which results from the action of hypochlorous acid upon *iso*butylene (Butlerow, Annalen, 1867, **144**, 24). Is formed in small quantity by the action of elliptical yeast upon sugar or glycerol (Claudon and Morin, Compt. rend. 1887, **104**, 1187); by the reduction of *iso*butaldehyde with sodium amalgam (Linnemann and Zotta, Annalen, 1872, **162**, 11).

Properties.—Colourless liquid, soluble in 10 5 parts of water, from which calcium chloride causes it to separate. Smells like fusel oil. Is oxidised by chromic acid into *iso*butyric acid, acetic acid, carbon dioxide, acetone, and other products (Krämer, Ber. 1874, **7**, 252; Schmitt, *ibid.* **8**, 1361). On distillation with zinc dust it loses the elements of water and yields *iso*butylene (Jahn, *ibid.* 1880, **13**, 989).

Treated with iodine and aluminium, aluminium tri*iso*butoxide $Al(C_4H_9O)_3$ is formed, a liquid which may be distilled *in vacuo* (Gladstone and Tribe, J.C.S. 1881, **39**, 6; Tistshenko, *l c*).

*Iso*butyl alcohol may be catalytically oxidised to *iso*butaldehyde A yield of 50% is obtained when the vapour of the alcohol mixed with air is passed over warm freshly reduced copper spirals and the products collected (E. Orloff, J S C.I. 1908, **27**, 957).

When chlorine is passed into dry *iso*butyl alcohol, and the solution subsequently heated gently, the product can be separated into two fractions, b p. 80°–100° and 170°–250° respectively. The lower fraction consists of *chloroiso butaldehyde*, b p 90°–91°; d_4^{15} 1·186. It combines with sodium hydrogen sulphite, and when oxidised with alkaline permanganate yields acetone and hydroxy*iso*butyric acid, $Me_2C(OH)CO_2H$, m p. 78°. A termolecular polymeride, $C_{12}H_{21}Cl_3O_3$, which melts at 107°, is obtained by shaking with strong sulphuric acid (A. Brochet, Compt. rend 1892, **114**, 1538). If the alcohol is kept cold, the chief product is *αβ-dichloroisobutyl* iso*butyl ether*, $CMe_2Cl{\cdot}CHCl\ O{\cdot}CH_2{\cdot}CHMe_2$, b p. 192 5°/760 mm, d_4^{15} 1 031. Water is without action on this product at low temperatures, but at 100° produces hydrogen chloride and α chloroiso-butaldehyde and di*iso*butylmonochloro*iso*butyral $CMe_2Cl{\cdot}CH(OC_4H_9)_2$, b.p. 218°, d_4^{15} 0 9355 (A. Brochet, Compt. rend. 1894, **118**, 1280; *see also* Brochet, Bull. Soc. chim. 1896, [iii], **15**, 16; *ibid.* 20).

When chlorine is led into hot *iso*butyl alcohol, *iso*butyl chloro*iso*butyrate, *iso*butyl *αβ*-dichloro*iso*butyrate, mono- and dichloro*iso*butaldehyde, *iso*butyric acid, oxy*iso*butyric acid, crotonic acid, CO, CO_2 and methyl chloride are produced. Treating aqueous *iso*butyl alcohol with chlorine water produces *iso*butyric acid, and *iso*butyl α-chloro*iso*butyrate (Brochet, Ann Chim. Phys. 1897, [vii], **10**, 363).

*Iso*butyl alcohol, when acted on by bromine, readily yields *iso*butyl bromide, mixed with *iso*butyl *iso*butyrate, and bromo*iso*butaldehyde (Étard, Compt. rend. 1892, **114**, 753).

Kutzelnigg (Z. anal. Chem. 1929, **77**, 349) has shown that *iso*butyl alcohol gives a characteristic orange colour with potassium ferrocyanide.

(For combinations and derivatives of *iso*butyl alcohol, *v.* Gladstone and Tribe, J C.S. 1881, **39**, 6; Pierre and Puchot, Annalen, 1872, **163**, 274; and Heindl, Monatsh. 1881, **2**, 208.)

3. *Secondary butyl alcohol*, 2 *hydroxybutane*, *methyl ethyl carbinol*,

$\begin{matrix}C_2H_5\\CH_3\end{matrix}{>}CH{\cdot}OH$; b.p. 99° at 738·8 mm. (Lieben, Annalen, 1869, **150**, 114); 99 5° (Brunel *et al*), sp gr. 0 827 at 0°, 0·810 at 22° (L.).

Formed by the action of water upon the compound of zinc ethyl and aldehyde:

$$MeEtCH\ O\ ZnEt+H_2O = EtMeCH{\cdot}OH+ZnO+C_2H_6$$

(Wagner, Annalen, 1876, **181**, 261). Also by

acting upon secondary butyl iodide with silver acetate and saponifying the resulting acetate by means of potash, or by hydration of butenes in the presence of sulphuric acid, phosphoric acid, or benzenesulphonic acid. The crude product is separated by fractionation (Canad. P. 202135; B.P. 161591; U.S.P. 1408320). Normal butyl alcohol may be changed into the secondary alcohol; the normal iodide is heated with potash, and the normal butylene so obtained on treatment with hydriodic acid yields secondary butyl iodide (Saytzeff, Z. anal. Chem. 1870, **9**, 327). It may also be prepared from the normal isomeride by treating *n*-butylamine with nitrous acid (Meyer, Ber. 1877, **10**, 130; Kanonnikoff and Saytzeff, J.C.S. 1875, **28**, 626).

Properties.—Liquid, with strong odour; upon oxidation yields methyl ethyl ketone, and acetic acid (Kanonnikoff and Saytzeff, *l.c.*). Heated with a trace of hydrochloric, hydrobromic, or hydriodic acid, in a sealed tube, to 240°, yields C_4H_8 (*ψ*-butylene). It has been separated into its optical antipodes by R. Meth (Ber. 1907, **40**, 695), through the brucine salts of the acid sulphate. Viditz has separated the optical isomerides through the brucine salts of the acid phthalate (Biochem. Z. 1933, **259**, 294). *d-sec-*Butyl alcohol has $[\alpha]_D^{20}+13{\cdot}87$ (Pickard and Kenyon, J.C.S. 1913, **103**, 1925).

4. *Tertiary butyl alcohol, trimethyl carbinol,* $(CH_3)_3C{\cdot}OH$. A solid; m.p. 25·45° (De Forcrand, Compt. rend. 1903, **136**, 1034); b.p. 82·94° (corr.) (Linnemann, Annalen, 1872, **162**, 26); 81·5°–82° (Perkin, J.C.S. 1884, **45**, 468); 82·25° (Thorpe and Rodger, Phil. Trans. 1894, A. **185**, 539). Sp.gr. 0·7792 at 37° (L.); 0·7788 at 30° (Butlerow, Annalen, 1872, **162**, 229); 0·7864 at 20°/4°; 0·7802 at 26°/4° (Brühl, Annalen, 1880, **203**, 17); 0·7836 at 25°/25°, 0·7761 at 35°/35°; mol. magn. rotation at 24·3°=5·122 (P.); n_D^{20} 1·38779 (Brühl); crit. temp.=234·9° (Pawlewski, Ber. 1883, **16**, 2634).

Formed from *iso*butyl iodide by treatment with acetic acid and silver oxide (Linnemann, *l.c.*; Butlerow, Annalen, 1873, **168**, 143); also from *iso*butylamine by treatment with nitrous acid, and from *iso*butyl carbimide $CON{\cdot}C_4H_9$, by action of potash (Linnemann, Annalen, 1872, **162**, 12). Can be prepared by allowing 20 g. of tertiary butyl iodide and 50 g. of water to stand in contact for two or three days (Dobbin, J.C.S. 1880, **37**, 238).

*Iso*butyl alcohol heated with excess of hydrochloric acid yields a mixture of secondary and tertiary butyl chlorides, the latter only is hydrolysed when the mixture is heated with six volumes of water yielding the alcohol (Freund, J. pr. Chem. 1875, [ii], **12**, 25).

Properties.—Forms rhombic plates or prisms. Unites with water to form a liquid hydrate, $2C_4H_{10}O,H_2O$ (b.p. 80°; sp.gr. 0·8276 at 0°) (Butlerow, Annalen, 1872, **162**, 229; *cf.*, however, Young and Fortey, J.C.S. 1902, **81**, 729).

The existence of a hydrate, $C_4H_{10}O,2H_2O$, m.p. 0°, is established by cryoscopic, density, and viscosity determinations (Paternò and Mieli, Atti R. Accad. Lincei, 1907, (v), **16**, ii, 153).

In sunlight it combines with chlorine, forming tertiary butyl chloride and other substances (D'Otreppe, Jahresber. 1881, 512).

Trimethyl carbinol explodes feebly when treated with bromine, yielding *isobutylene bromide,* $C(CH_3)_2Br{\cdot}CH_2Br$, boiling at 148° (Etard, Compt. rend. 1892, **114**, 753).

Tertiary butyl alcohol has a slightly narcotic action when taken internally, and is found in the urine in combination with glycuronic acid (Thierfelder and v. Mering, Chem. Soc. Abstr. 1885, i, 1002).

Nitrohydroxybutanes may be obtained quantitatively as follows: By the action of nitromethane on formaldehyde, in presence of a little potassium carbonate, tertiary nitrotrihydroxybutane, $O_2N{\cdot}C(CH_2{\cdot}OH)_3$, a white crystalline solid, melting at 158°–159°, is produced. Nitroethane produces tertiary nitrodihydroxybutane, $NO_2{\cdot}C(CH_3)(CH_2OH)_2$, melting at 139°–140°. Secondary nitropropane yields nitro*iso*butyl alcohol, $NO_2{\cdot}C(Me)_2{\cdot}CH_2OH$, melting at 82° (L. Henry, Compt. rend. 1895, **121**, 210).

Butyl Bromides. Tetryl bromides, C_4H_9Br.

1. *Normal butyl bromide, a-bromobutane,*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br;$$

b.p. 99·88° (corr.) (Linnemann, Annalen, 1872, **161**, 193); sp.gr. 1·3050 at 0°, 1·2792 at 20°, 1·2571 at 40° (Lieben and Rossi, *ibid.* 1871, **158**, 161).

Formed from normal butyl alcohol and hydrobromic acid (L. and R. Taboury, Bull. Soc. chim. 1911 [iv], **9**, 124). It is best prepared in quantity by treating a mixture of bromine (400 g.) and ice (425 g.) with sulphur dioxide until reduced and then adding *n*-butyl alcohol (296 g.) and conc. sulphuric acid (200 g.). The mixture is refluxed and the product fractionated (Kamm and Marvel, J. Amer. Chem. Soc. 1920, **42**, 299).

By the action of bromine, *aβ*-dibrombutane (b.p. 166°) is formed (Linnemann, Annalen, 1872, **161**, 190).

2. iso*Butyl bromide, a-bromo-β-methyl propane* $(CH_3)_2CH{\cdot}CH_2Br$; b.p. 92·3° (corr.) (Linnemann, *ibid.* **162**, 34); *cf.* Perkin (J.C.S. 1884, **45**, 459); 91·7° (corr.) (Thorpe); sp.gr. 1·2038 at 16° (L.), 1·2722 at 15°/15°, 1·2598 at 25°/25° (P.). Molecular rotation= 8·003 at 16·2° (P.). From *iso*butyl alcohol, bromine, and phosphorus (Wurtz, Annalen, 1855, **93**, 114). Unites with bromine at 150° to form $C_4H_7Br_3$ (L.). Pure *iso*butyl bromide is an unstable substance yielding the tertiary isomer when heated above the b.p. It yields a solid piperidide, m.p. 134°–135° (Powell and Dehn, J. Amer. Chem. Soc. 1917, **39**, 1717).

3. *Tertiary butyl bromide, β-bromo-β-methyl propane,* $(CH_3)_3CBr$; b.p. 72° at 761·5 mm.; sp.gr. 1·215 at 20° (Roozeboom, Ber. 1881, **14**, 2396), 1·2020 at 15°/15°, 1·1892 at 25°/25°; mol. magn. rotation=8·238 at 17·8° (P.). Formed when *iso*butyl bromide is heated to 240° (Eltekow, Ber. 1875, **8**, 1244). Also from trimethyl carbinol and phosphorus pentabromide (Reboul, Jahresber. 1881, 409). May also be prepared by leading *iso*butylene into a solution of hydrobromic acid of sp.gr. 1·7 (Roozeboom, *l.c.*). Is readily decomposed at 300° into *iso*butylene and hydrobromic acid. Water, in the cold, forms the alcohol.

Tribromo-tert-*butyl alcohol* (brometone), $C_4H_7OBr_3$, m.p. 167°–176°, forms white

crystals, has a camphor like taste and odour, is slowly volatile in air, and can be distilled with steam (Aldrich, J. Amer. Chem. Soc. 1911, 33, 386). For pharmacological properties, *see* Houghton and Aldrich, Proc. Amer. Physiol. Soc. 1902. The alcohol may be esterified by treatment with propionyl or butyryl chlorides (Aldrich, J. Amer. Chem Soc. 1918, 40, 1948)

4. *Secondary butyl bromide, β bromobutane,* $CH_3\cdot CH_2\cdot CHBr\cdot CH_3$; b p. 90°–93° (V. Meyer and Müller, J. pr. Chem 1892, [ii], 46, 183); obtained from secondary butyl alcohol by the action of hydrobromic acid, and yields βγ-dibrombutane by warming with iron and bromine.

For observations on the course of the intra molecular transformations of the butyl bromides and chlorides, *see* Michael and Leupold, Annalen, 1911, 379, 263; Michael and Zeidler, Annalen, 1912, 393, 81; Michael, Scharf and Voigt, J. Amer. Chem Soc. 1916, 38, 653 Franke and Dworzak (Monatsh. 1923, 43, 661) have prepared optically active *sec*-butyl bromide, b.p. 89°–91°; $[\alpha]_D$ +6·36°.

Butyl Chlorides. Tetryl chlorides, C_4H_9Cl.

1. *Normal butyl chloride, α-chlorbutane,*

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2Cl,$$

b p. 77 96° (corr) (Linnemann, Annalen, 1872, 161, 197), sp gr. 0 9074 at 0°, 0 8874 at 20° (Lieben and Rossi, *ibid.* 1871, 158, 161); 0 9074 at 0° (L). Formed by the action of chlorine upon *n*-butane (Pelouze and Cahours, Jahresber. 1863, 524), more easily by the action of hydrochloric acid upon *n*-butyl alcohol (Lieben and Rossi). It is best prepared by refluxing a mixture of the alcohol with aqueous hydrochloric acid in the presence of zinc chloride. The product is refluxed with sulphuric acid to remove impurities and re-distilled (Norris and Taylor, J. Amer. Chem. Soc. 1924, 46, 753).

2. iso*Butyl chloride, β methyl α-chlorpropane,* $(CH_3)_2CH\cdot CH_2Cl$; b p. 68 5° (Linnemann, Annalen, 1872, 162, 17); 68 5°–69° (Perkin, J.C.S. 1884, 45, 451); 69 02° (corr.) (Thorpe); sp gr. 0 8798 at 15° (L.), 0 8953 at 0°, 0·8651 at 27·8°, 0 8281 at 59° (Pierre and Puchot, Annalen, 1872, 163, 276), 0 8835 at 15°/15°, 0 8739 at 25°/25° (P.). Molecular rotation at 21·3°=6·144 (Perkin). Formed by the action of hydrochloric acid or PCl_5 upon the alcohol (Wurtz, *ibid.* 1855, 93, 113). By the action of chlorine, hexachlorbutane is produced.

*iso*Butyl chloride is also produced by the interaction of chlorine and *iso*butane in diffused sunlight (Mabery and Hudson, Amer. Chem. J. 1897, 19, 245); and also by treating *iso*butylamine cooled to −15° with nitrosyl chloride (Solonina, Chem. Zentr. 1898, ii. 887).

3. *Tertiary butyl chloride, β-methyl-β-chlorpropane* $(CH_3)_3CCl$; b.p. 51°–52° (Perkin, J.C S. 1884, 45, 451); sp. gr. 0 8471 at 15°/15°, 0·8368 at 25°/25°; molecular rotation at 15°=6·257 (Perkin).

Formed (1) by the chlorination of tertiary butane (Butlerow); (2) by the action of iodine monochloride upon *iso*butyl iodide (Linnemann, Annalen, 1872, 162, 18); (3) by the action of hydrochloric acid upon *iso*butylene at 100° (Zalessky, Ber. 1872, 5, 480; Le Bel, Bull Soc chim. 1877, [ii], 28, 462); (4) by saturating trimethyl carbinol at 0° with hydrogen chloride (Schramm, Monatsh. 1888, 9, 619). *See also* "Organic Syntheses," Vol. VIII, p. 50.

tert-Butyl chloride is also formed by the action of PCl_5 on trimethyl carbinol (Janschenko, Chem. Zentr. 1897, ii, 334), and produced, together with *iso*butyl chloride, by the action of nitrosyl chloride on tertiary butylamine in xylene solution at −15° to −20° (Salonina, *ibid.* 1898, ii, 888).

tert-Butyl chloride, when heated with five or six vols. of water to 100°, yields the alcohol (Butlerow, Annalen, 1867, 144, 33). Chlorine in diffused daylight, in the cold, forms $C_4H_8Cl_2$ (b p 106°–107°), $C_4H_7Cl_3$ and $C_4H_5Cl_5$, whilst in direct sunlight $C_4H_4Cl_6$ (b.p. in partial vacuum about 115°), and other products are formed (D'Otreppe de Bouvette, Jahresb. 1882, 441).

4. *Secondary butyl chloride, β-chlorbutane,* $CH_3\cdot CH_2\cdot CHCl\cdot CH_3$, is produced by the action of nitrosyl chloride on secondary butylamine in xylene solution at −20° (Solonina, Chem Zentr. 1898, ii, 888).

Butyl Cyanates. Only the *iso* cyanates have been described.

1. iso*Butyl isocyanate, iso*butyl carbimide $(CH_3)_2CH\cdot CH_2\cdot NCO$; b p. 110°, obtained by the distillation of *iso*butyl iodide with silver cyanate and sand (Brauner, Ber. 1879, 12, 1877).

2 *Tertiary butyl isocyanate,*

$$(CH_3)_3C\cdot NCO;$$

b p. 85 5° (corr.); sp gr. 0 8676 at 0°; remains liquid at −25°. Is formed, together with other substances, when silver cyanate acts upon *iso*butyl iodide (Brauner, Ber. 1879, 12, 1874). By the action of hydrochloric acid, it yields tertiary butylamine, $(CH_3)_3C\cdot NH_2$. Potash produces symmetrical di*iso*butyl urea, melting at 242°.

Butyl Cyanides. $C_4H_9\cdot CN$.

1. *Normal butyl cyanide, valeronitrile,*

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN;$$

b p. 140 4° at 739 3 mm.; sp gr. 0 8164 at 0° (Lieben and Rossi, Annalen, 1871, 158, 171). This may readily be prepared by treating *n*-butyl bromide (1,575 g.) in 1,575 c.c. ethyl alcohol (95%) with a solution of powdered sodium cyanide (690 g.) in 690 c.c. water The mixture is heated under reflux on the water bath and finally fractionated. Yield 720–726 g., b.p. 138°–141° (Adams and Marvel, J. Amer. Chem. Soc. 1920, 42, 310).

On alkaline hydrolysis, valeric acid is formed, whilst hydrolysis with an acid in alcoholic solution yields ethyl valerate.

2. iso*Butyl cyanide* $(CH_3)_2\cdot CH\cdot CH_2\cdot CN$; b.p. 126°–128° at 714 mm. (Erlenmeyer and Hell, Annalen, 1871, 160, 266); 129 3°–129 5° at 764 3 mm. (R. Schiff, Ber. 1886, 19, 567); sp. gr. 0 8227 at 0°, 0 8069 at 20° (Erlenmeyer and Hell); 0 6921 at 129°/4° (S). Formed by the oxidation of gelatin (Schlieper, Annalen, 1846, 59, 15) or casein (Guckelberger, *ibid.* 1848, 64, 76) with chromic acid; also by the action of P_2O_5 upon ammonium *iso*valerate (Dumas,

Malaguti, and Leblanc, *ibid.* 1848, **64**, 334). May be prepared by heating 300 g. *iso*butyl iodide, 98 g. of potassium cyanide, 98 g. of alcohol, and 25 g. of water for three days on the water-bath (Erlenmeyer and Hell, *l.c.*).

3. *Tertiary butyl cyanide* $(CH_3)_3C{\cdot}CN$; m.p. 15°–16°; b.p. 105°–106°. Prepared by mixing 100 parts of tertiary butyl iodide, 110 parts of mercury potassium cyanide, with 75 parts of talc, and allowing the mixture to remain for two or three days at a temperature not exceeding 5°. The mass is then treated with water, and distilled on the paraffin-bath (Butlerow, Annalen, 1873, **170**, 154).

4. *Secondary butyl cyanide*, methylethylacetonitrile, $EtCHMe{\cdot}CN$; b.p. 125°; sp.gr. 0·8061 at 0°. Sodium ($\frac{1}{2}$ eqv.) is dissolved in propionitrile in benzene, and ethyl iodide (1 eqv.) added (Hanriot and Bouveault, Bull. Soc. chim. 1889, [iii], **1**, 172).

Butyl Hydrides. Butanes, tetranes.

1. *Normal butane, diethyl, a-methylpropane,*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3;$$

b.p. 1° (Butlerow, Z. Chem. 1867, 363); –0·3°, Burrell and Robertson (J. Amer. Chem. Soc. 1915, **37**, 2188); sp.gr. 0·60 at 0° (Ronalds, J.C.S. 1865, **18**, 54). Critical temp. 153·2°; critical press. 35·67 atm. Occurs in crude petroleum (Ronalds, *l.c.*; Lefebvre, Z. Chem. 1869, 185), and also in natural gas (Garner, Amer. Gas Eng. J. 1908, **108**, 489). Formed by heating ethyl iodide with zinc to 150° (Frankland, Annalen, 1849, **71**, 173; Schöyen, *ibid.* 1864, **130**, 233). Also by the action of sodium amalgam upon ethyl iodide (Löwig, Jahresb. 1860, 397). A colourless gas, insoluble in water. 1 vol. of alcohol at 14·2° and 744·8 mm. absorbs 18·13 vols. of butane (Frankland). Liquid butane polymerises quantitatively to naphthenes in the presence of aluminium chloride (U.S.P. 1395620).

Butane has recently found application in the United States as a substitute for ammonia in refrigeration. It has the advantages of being non-poisonous and non-corrosive, although these are somewhat reduced by the hazard of fire (Edwards, Amer. Soc. Refrig. Eng. J. 1922, **8**, 488; Nuckolls, Amer. Chem. Abstr. 1925, **19**, 1777).

2. iso*Butane, trimethylmethane*, $(CH_3)_3CH$. Formed by heating 0·9 part of *iso*butyl iodide with 2·4 parts of aluminium chloride to 120° in a sealed tube from which air is excluded (Köhnlein, Ber. 1883, **16**, 562). Also by the action of zinc and water upon *tert*-butyl iodide (Butlerow, Annalen, 1867, **144**, 10). The gas is readily soluble in alcohol, from which it can be expelled by dilution with water, b.p. –13·4°; critical temp. 133·7°; critical press. 36·54 atm. (Seibert and Burrell, J. Amer. Chem. Soc. 1915, **37**, 2691). Vapour pressure may be represented by the formula:

$$\log P = -1632{\cdot}661/T + 1{\cdot}75 \log T - 0{\cdot}0158873T + 9{\cdot}06814$$

(Burrell and Robertson, *ibid.* 2482).

3. cyclo*Butane, tetramethylene*, $\begin{array}{l} CH_2{-}CH_2 \\ | \quad\quad\;\; | \\ CH_2{-}CH_2 \end{array}$

b.p. 11–12°/760 mm., d_4^0 0·703; n_D 1·37520. The gas, which has a very faint odour, was prepared by passing *cyclo*butene and hydrogen over nickel at 100°. It is not affected by cold HI or $KMnO_4$ solutions. At 200° it is reduced to butane by hydrogen in the presence of nickel (Willstätter and Bruce, Ber. 1908, **40**, 3979).

Metallic Derivatives. Some work has been done on the preparation of the butyl derivatives of various metals. Lead tetra-*iso*-butyl, a liquid, is described by Grüttner and Kranse (Ber. 1917, **50**, 278), while di-*n*- and di-*iso*-butyl thallic halides have been obtained by Kranse and Grosse (*ibid.* 1925, **58**, [B], 1933) by treatment of the alkyl halide with an ethereal solution of the thallic salt.

Butyl Iodides. C_4H_9I.

1. *Normal butyl iodide,*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2I;$$

b.p. 129·8° (corr.) (Linnemann, Annalen, 1872, **161**, 196); 130·4°–131·4° at 745·4 mm. (Brühl, *ibid.* 1880, **203**, 21); sp.gr. 1·643 at 0°, 1·6136 at 20° (Lieben and Rossi, *ibid.* 1871, **158**, 163), 1·6166 at 20°/4° (Brühl). Prepared from *n*-butyl alcohol and hydriodic acid (Linnemann, *l.c.*). Adams and Voorhees (J. Amer. Chem. Soc. 1919, **41**, 789) have developed a method of preparation suitable for large-scale work using the alcohol and iodine in the presence of a mixture of red and yellow phosphorus. By the action of iodine trichloride at 250° it yields hexachlorethane, C_2Cl_6 (Kraft, Ber. 1877, **10**, 806).

2. iso*Butyl iodide, a-iodo-β-methylpropane,*

$$(CH_3)_2{\cdot}CH{\cdot}CH_2I;$$

b.p 120·0° (corr.) (Linnemann, Annalen, 1871, **160**, 240; **192**, 69); 83°–83·25° at 250 mm. (Perkin, J.C.S. 1884, **45**, 451); 119·94° (Thorpe and Rodger, Phil. Trans. 1894, A, **11**, 470); sp.gr. 1·6401 at 0° (L.), 1·6056 at 20°/4° (Brühl, Annalen, 1880, **203**, 21), 1·61385 at 15°/15°, 1·60066 at 25°/25° (P.), n_D^{20} 1·49975 (Karvonen, Ann. Acad. Sci. Fennicæ, [A], **5**, No. 6, 124). Prepared from *iso*butyl alcohol, phosphorus, and iodine (Wurtz, Annalen, 1855, **93**, 116).

3. *Secondary butyl iodide, β-iodobutane,*

$$C_2H_5{\cdot}CHI{\cdot}CH_3;$$

b.p. 117°–118° (Luynes, Bull. Soc. chim. 1864, [ii], 2, 3); 119°–120° (Lieben, Annalen, 1869, **150**, 96); sp.gr. 1·6263 at 0°/0°, 1·5952 at 20°/0°, 1·5787 at 30°/0° (Lieben). Formed by distilling erythritol with hydriodic acid (Luynes) or from *n*-butylene and hydriodic acid (Wurtz, Annalen, 1869, **152**, 23). (*See also* Clarke, Chem. Zentr. 1908, ii, 1015.)

4. *Tertiary butyliodide, β-methyl-β-iodopropane,* $(CH_3)_3CI$; b.p. 98°–99° (with decom.) (Butlerow); 100·3° (Puchot, Ann. Chim. Phys. 1883, [v], **28**, 546); sp.gr. 1·571 at 0°, 1·479 at 53° (P.). Prepared from tertiary butyl alcohol and hydriodic acid or from *iso*butylene and hydriodic acid (Butlerow, Annalen, 1867, **144**, 5, 22); is easily decomposed (by silver oxide, potash, or by heating with zinc and water), into hydriodic acid and *iso*butylene (Butlerow, Z. Chem. 1867, 362). Is also decomposed by water in the cold, yielding hydriodic acid and tertiary butyl alcohol. On heating with sodium, it yields a mixture of hydrogen, *iso*butylene, and tri*iso*-

butylene ($C_{12}H_{24}$) (Dobbin, J.C.S. 1880, **37**, 236).

Butyl Mercaptans. $C_4H_9\cdot SH$.

1. *Normal butyl mercaptan,*

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot SH;$$

b.p. 97°–98°; sp.gr. 0.858 at 0° (Saytzeff and Grabowsky, Annalen, 1874, **171**, 251; 1875, **175**, 351).

2. iso*Butyl mercaptan,*

$$(CH_3)_2CH\cdot CH_2\cdot SH,$$

b.p. 88°; sp.gr. 0.848 at 11.5° (Humann, Annalen, 1855, **95**, 256), 0.83573 at 20°/4° (Nasini, Ber. 1882, **15**, 2882). Esterification with acetic acid at 200° reaches an equilibrium at a concentration of 12% ester (Faber and Reid, J. Amer. Chem. Soc. 1917, **39**, 1930).

3. *Secondary butyl mercaptan,*

$$C_2H_5\cdot CH(SH)CH_3;$$

b.p. 84°–85°, sp.gr. 0.8299 at 17°, from the corresponding iodide and alcoholic potassium hydrosulphide (Levene and Mikeska, J. Biol. Chem. 1925, **63**, 85). Oxidation with nitric acid yields the β sulphonic acid. The mercury compound $(C_4H_9S)_2Hg$ melts at 189° (Reymann, Ber. 1874, **7**, 1287).

4. *Tertiary butyl mercaptan,*

$$(CH_3)_3C\cdot SH,$$

is prepared from tertiary butyl iodide, zinc sulphide, and alcohol (Dobbin, J.C.S. 1890, **57**, 641). It boils at 63.7°–64.2°, and solidifies in a freezing mixture. The metallic derivatives are described by Rheinboldt *et al.* (J. pr. Chem. 1932, [ii], **134**, 257).

Butyl Nitrates.

1. *Normal butyl nitrate,*

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot O\cdot NO_2,$$

boils at 136°, sp.gr. 1.048 at 0° (Bertoni, Gazzetta, 1890, **20**, 374).

2. iso*Butyl nitrate,* $(CH_3)_2CH\cdot CH_2\cdot O\cdot NO_2$, mol. magn. rotation at 8.9°=5.18; b.p. 123.5–124.5°; sp.gr. 1.0334 at 4°/4°, 1.0264 at 10°/10°, 1.0124 at 25°/25° (Perkin, J.C.S. 1889, **55**, 684); $n_D^{23.3}$ 1.40130 (Brühl, Z. physikal. Chem. 1895, **16**, 214). Prepared from silver nitrate, urea, and *iso*butyl iodide (Wurtz, Annalen, 1855, **93**, 120; Chapman and Smith, Z. Chem. 1869, 433).

3. *Secondary butyl nitrate* boils at 124°; sp.gr. 1.0382 at 0° (Bertoni, Gazzetta, 1890, **20**, 375).

Butyl Nitrites, Nitrobutanes, $C_4H_9NO_2$.

1. n-*Butyl Nitrite,* b.p. 75°–76°, has been prepared by Sugden, Reed and Wilkins (J.C.S. 1925, **127**, 1525).

2. Iso*Butyl nitrite,* $(CH_3)_2CH\cdot CH_2\cdot NO_2$; b.p. 67°; sp.gr. 0.89445 at 0° (Chapman and Smith, Z. Chem. 1869, 433), 0.8878 at 4°/4°, 0.8806 at 10°/10°, 0.8752 at 15°/15°, 0.8702 at 20°/20°, 0.8652 at 25°/25°; mol. magn. rotation at 8.2°=5.51 (Perkin, J.C.S. 1889, **55**, 686, 757); $n_D^{21.1}$ 1.37151 (Brühl, *l.c.*). Prepared by mixing *iso*butyl alcohol and sulphuric acid, and gradually pouring the cooled mixture into an aqueous solution of sodium nitrite (1 : 3); the upper layer, consisting of *iso*butyl nitrite, is decanted, washed with potassium carbonate solution, and dried. It is a pale yellow liquid, apt to become acid by keeping when rapid decomposition sets in. Taken medicinally, it lowers the blood pressure and produces respiratory paralysis (Dunstan and Woolley, Pharm. J. 1888–1889, [iii], **19**, 487).

3. *Tertiary butyl nitrite,* $(CH_3)_3C\cdot NO_2$; b.p. 63°; sp.gr. 0.8914 at 0° (Bertoni, Gazzetta, 1885, **15**, 351); 67°–68° (Tschermak, Annalen, 1876, **180**, 155). From the alcohol and glyceryl nitrite (B.); also from the iodide and silver nitrite (T.). A yellow, mobile liquid; soluble in alcohol, ether and chloroform; sparingly soluble in water.

Butyl Derivatives of Aromatic Nitrohydrocarbons.

The butyl derivatives of many aromatic nitrohydrocarbons have a musk like odour, and are sold as "artificial musk." *Musk Baur,* trinitro *m tert*-butyltoluene,

$$C_6H(CH_3)(NO_2)_3C(CH_3)_3,$$

is made by nitrating *m tert*-butyltoluene with fuming nitric and fuming sulphuric acids. *tert*-Butyltoluene is prepared by Friedel and Craft's method, as described below, by the action of *tert*-butyl bromide on toluene in the presence of aluminium chloride. Butylbenzene, ethylbenzene, and xylene are formed at the same time.

An unsymmetrical butylcresol is formed by adding butyl alcohol and zinc chloride to *m*-cresol. When etherified and nitrated, it possesses the odour of civet (A. Baur, J.S.C.I. 1892, **11**, 307; Dingl. poly. J. 1889, **273**, 522; J.S.C.I. 1894, **13**, 1218).

Butylxylene may be prepared by passing a current of *iso*butylene gas through a mixture of 5 kilos. *m*-xylene, 50 g. *iso*butyl chloride, and 200 g. aluminium chloride at 10°. The product is washed with water, and the fraction of the oil boiling at 200°–302° collected. *Gaseous* hydrogen chloride and hydrogen bromide may be employed to start the reaction (A.-G. fur Anilin-Fabr., F.P. 372603).

Butyl Ethers, $(C_4H_9)_2O$.

1. *Normal butyl ether*; b.p. 140.5° at 741.5 mm. (Lieben and Rossi, Annalen, 1873, **165**, 110); sp.gr. 0.784 at 0°, 0.7685 at 20° (L. and R.), 0.7865 at 0° (Dobriner, Annalen, 1888, **243**, 8). It may be prepared by the action of the sodium derivative of the alcohol upon *n*-butyl bromide (Reboul, Compt. rend. 1889, **108**, 39); or in quantity by heating butyl alcohol with 10–15% of its weight of sulphuric acid and distilling slowly (Popelier, Bull. Soc. chim. Belg. 1923, **32**, 139); Senderens (Compt. rend. 1925, **181**, 698), however, advocates the use of 25% of sulphuric acid.

The use of this ether in Grignard reactions, particularly if an elevated temperature is desired, has been recommended by Gilman (J. Amer. Chem. Soc. 1928, **50**, 2810).

2. iso*Butyl ether* $[(CH_3)_2CH\cdot CH_2]_2O$; b.p. 122°–122.5°; sp.gr. 0.7616 at 15°. From *iso*butyl bromide and sodium *iso*butylate. The action of *iso*butyl iodide upon potassium *iso*butylate—which, according to Wurtz, yields this ether—really gives a mixture of di*iso*butylene

and *iso*butyl alcohol (Reboul, Compt. rend. 1889, **108**, 162).

3. *Secondary butyl ether*,

$[C_2H_5\cdot CH(CH_3)]_2O$;

b.p. 120°–121°; sp.gr. 0·756 at 21°. From ethylidene chlorhydrin, and zinc ethyl (Kessel, Annalen, 1875, **175**, 50). Formed in mere traces only by the action of secondary butyl bromide upon the sodium derivative of the secondary alcohol (Reboul, *l.c.*). Reboul obtained also the following mixed ethers:

sec-Butyl *iso*butyl ether; b.p. 121°–122°; sp.gr. 0·7652 at 21°;

n-Butyl *iso*butyl ether; b.p. 131·5°; sp.gr. 0·763 at 15·5°;

n-Butyl *sec*-butyl ether; b.p. 131°; sp.gr. 0·7687 at 15°;

n-Butyl *tert*-butyl ether; b.p. 124°; but could not obtain the secondary tertiary, and the ditertiary ethers (Bull. Soc. chim. 1889, [iii], **2**, 25).

Butyl sulphides.

1. *Normal butyl sulphide*,

$(CH_3\cdot[CH_2]_3)_2S$;

b.p. 182°; sp.gr. 0·8523 at 0° (Saytzeff, Annalen, 1874, **171**, 253). From butyl iodide and potassium sulphide. Gray and Gutekunst (J. Amer. Chem. Soc. 1920, **42**, 856) heat a mixture of butyl alcohol and 20% oleum, neutralise the cooled product, and then distill with sodium sulphide. A mixture of *n*-butyl sulphide and mercaptan is produced, the former predominating. Fuming nitric acid yields the sulphone $(C_4H_9)_2SO_2$, (m.p. 43·5°) (Grabowsky, Annalen, 1875, **175**, 348). Nitric acid of sp.gr. 1·3 converts it into the oxide $(C_4H_9)_2SO$, melting at 32°.

n-*Butyl Sulphone* has also been prepared by oxidation of the sulphoxide obtained by the action of thionyl chloride on butyl magnesium bromide (Bert, Compt. rend. 1924, **178**, 1826).

2. iso*Butyl sulphide* $[(CH_3)_2CH\cdot CH_2]_2S$; b.p. 172°–173° at 747 mm. (Grabowsky and Saytzeff, Annalen, 1874, **171**, 254), 170·5° at 752 mm. (Beckmann, J. pr. Chem. 1878, [ii], **17**, 445); sp.gr. 0·8363 at 10° (B.). It is oxidised to the sulphone by action of alkaline hypochlorite solution (Birch and Norris, J.C.S. 1925, **127**, 1934).

iso*Butyl disulphide*, $(C_4H_9)_2S_2$; b.p. 220° (Spring and Legros, Ber. 1882, **15**, 1940).

3. *Secondary butyl sulphide*,

$(CH_3\cdot CH\cdot C_2H_5)_2S$;

b.p. 165°; sp.gr. 0·8317 at 23° (Reymann, Ber. 1874, **7**, 1288).

n-Butyl Telluride, $(C_4H_9)_2Te$, has been prepared by Burstall and Sugden (J.C.S. 1930, 229). Its properties are fully described.

n-Butyl di-Selenide, $(C_4H_9)_2Se_2$, b.p. 129°–130°/13 mm., has been prepared by Backer and van Dam (Rec. Trav. chim. 1935, **54**, 531).

Butyl thiocarbimides. Butyl mustard oils; *iso*thiocyanates.

1. *Normal butyl thiocarbimide*,

$(C_4H_9)NCS$;

b.p. 167°. From *n*-butylamine, carbon disulphide, and alcohol (Hofmann, Ber. 1874, **7**, 512).

2. iso*Butyl thiocarbimide*,

$(CH_3)_2CH\cdot CH_2\cdot NCS$;

b.p. 162°; sp.gr. 0·9638 at 14° (Hofmann, Ber. 1874, **7**, 511).

3. *Secondary butyl thiocarbimide*,

$C_2H_5\cdot CH(CH_3)NCS$;

b.p. 159·5°; sp.gr. 0·944 at 12°. Occurs in the ethereal oil from spoonwort (*Cochlearia officinalis*) (Hofmann, Ber. 1869, **2**, 102; 1874, **7**, 512).

4. *Tertiary butyl thiocarbimide*,

$(CH_3)_3C\cdot NCS$;

m.p. 10·5°; b.p. 140° at 770·3 mm.; sp.gr. 0·9187 at 10°, 0·9003 at 34° (Rudnew, Bull. Soc. chim. 1880, [ii], **33**, 300). Has a pleasant aromatic odour.

BUTYLAMINES.

1. Monobutylamines.

(*a*) *Normal butylamine, a-aminobutane*,

$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$;

b.p. 75·5° at 740 mm. (Lieben and Rossi, Annalen, 1871, **158**, 172); sp.gr. 0·7553 at 0°, 0·7333 at 26° (L. and R.), 0·7401 at 20° (Linnemann and Zotta, Annalen, 1872, **162**, 3). Formed by the action of potassium hydroxide upon butyl cyanate (Lieben and Rossi); also from propyl cyanide by action of zinc and sulphuric acid (Linnemann and Zotta, Annalen, 1872, **162**, 3), or from nitrobutane by action of tin and hydrochloric acid (Züblin, Ber. 1877, **10**, 2083). It can be prepared from the alkyl halide and saturated ethyl alcoholic ammonia (Werner, J.C.S. 1919, **115**, 1010). It is miscible with water, and reduces copper, silver, and mercury solutions in presence of alkalis. The chloride forms a yellow crystalline compound with $PtCl_4$, which is almost insoluble in cold water. The degradation by nitrous acid has been investigated by Whitmore and Langlois (J. Amer. Chem. Soc. 1932, **54**, 3441) who found in addition to *n*- and *sec*-butyl alcohols, 36% of butenes.

(*b*) iso*Butylamine*, *a-amino-β-methylpropane*, $(CH_3)_2CH\cdot CH_2\cdot NH_2$; b.p. 68° (Schiff, Ber. 1886, **19**, 565), 68°–69° (Perkin, J.C.S. 1889, **55**, 694); sp.gr. 0·7357 at 55° (Linnemann, Annalen, 1872, **162**, 23), 0·7464 at 4°/4°, 0·7408 at 10°/10°, 0·7363 at 15°/15°, 0·7283 at 25°/25°; n_D^{17} 1·39878 (Brühl, Z. physikal. Chem. 1895, **16**, 214). From *iso*butyl cyanate and potash (Linnemann, Annalen, 1872, **162**, 23). From *iso*butyl iodide and ammonia (Hughes and Römer, Ber. 1874, **7**, 511); also from *iso*butyl chloride and ammonia dissolved in water or *iso*butyl alcohol, all three *iso*butylamines are produced, the tri*iso*butylamine in largest quantity. The bases can then be separated by means of ethyl oxalate. The product is first separated into two fractions, the one rich in the mono*iso*butylamine, the other rich in the di- and tri- compounds. To the former water and then ethyl oxalate are added; the primary base is thus converted into the oxamide $C_2O_2(NH\cdot C_4H_9)_2$, which is almost insoluble in boiling water, the secondary amine being changed into the ethyl oxamate,

$C_2H_5O\ C_2O_2{\cdot}N(C_4H_9)_2$. The other fraction (anhydrous) being poured into ethyl oxalate, the primary and secondary bases are converted into oxamates. The tertiary base is distilled off, and the oxamates are saponified by heating with slaked lime. The calcium oxamates can be separated by crystallisation, the di*iso*butyloxamate being the more soluble in alcohol, from which it separates in slender silky needles (Malbot, Compt. rend. 1887, **104**, 228).

*iso*Butylamine can be produced by heating *iso*butyl alcohol with ammoniacal zinc chloride to 260° (Merz and Gasiorowski, Ber. 1884, **17**, 624), or by the action of caustic potash (10% solution) upon a mixture of bromine and *iso*valeramide (equal molecules) at 60° (Hofmann, Ber. 1882, **15**, 769).

*iso*Butylamine mixes with water with contraction of volume and development of heat. A mixture of equal volumes of water and *iso*butylamine has a sp gr of 0 9002 at 15°/15°, instead of the calc density 0 8681 (Perkin, J.C.S. 1889, **55**, 696). With absolute alcohol and the amine similar results were obtained, the sp gr. of a mixture of equal volumes being 0 791 at 15°/15°, instead of 0 7632, the calculated number. The phosphotungstate has been described by Drummond (Biochem J. 1918, **12**, 5).

(*c*) *Secondary butylamine*,

$$C_2H_5{\cdot}CH(NH_2){\cdot}CH_3;$$

b.p. 63°; sp gr. 0 718 at 23° (Menschutkin, Chem. Zentr. 1898, i, 702). Formed by the action of potash upon secondary butyl cyanate, or of ammonia upon secondary butyl iodide (Hofmann, Ber. 1874, **7**, 513). Also by the action of dilute sulphuric acid upon secondary butyl mustard oil (Reymann, Ber. 1874, **7**, 1289).

By the reduction of methyl ethyl ketoxime by hydrogen and finely divided nickel at 160°–170°, secondary butylamine and di-secondary butylamine are produced. They are liquids, the latter boiling at 132°/758 mm. and forming an oxalate melting at 104° (Mailhe, Compt. rend. 1905, **141**, 113)

Secondary butylamine has been separated into its optical antipodes by Thomé (Ber. 1903, **36**, 582); $[\alpha]_D^{20}$ +7·44° and −7 40°.

(*d*) *Tertiary butylamine*, $(CH_3)_3C\ NH_2$; b.p. 45°; sp gr. 0 7137 at 0°, 0 7054 at 8°, 0 6931 at 15° (Rudnew, Bull. Soc Chim 1880, [ii] 33, 297; J.C.S.). Formed in small quantity by the action of potash upon *iso*butyl cyanate (Linnemann, Annalen, 1872, **162**, 19; Hofmann, Ber. 1874, **7**, 513). Also as a by-product in preparing trimethyl acetic acid from trimethyl carbinol iodide and mercuric cyanide (Rudnew).

2. **Dibutylamines.**

(*a*) *Di-normal butylamine*,

$$(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2)_2NH;$$

b p. 160°. Formed in small quantities by the action of potash upon butyl cyanate (Lieben and Rossi, Annalen, 1871, **158**, 175); also by the action of butyl chloride on ammonia (Berg, Ann. Chim. Phys. 1894, [vii], **3**, 294). The platinichloride forms yellow needles, almost insoluble in cold water.

(*b*) *Di-iso-butylamine*,

$$[(CH_3)_2CH{\cdot}CH_2]_2NH;$$

b.p. 139°–140°; sp gr. 0 7577 at 4°/4°, 0 7491 at 15°/15°, 0 7425 at 25°/25° (Perkin, J C.S. 1889, **55**, 697). From *iso*butyl bromide and alcoholic ammonia at 150° (Ladenburg, Ber. 1879, **12**, 949); also from *iso*butyl alcohol and ammoniacal zinc chloride at 270° (Merz and Gasiorowski, Ber. 1884, **17**, 627). The hydrochloride forms plates or leaflets easily soluble in alcohol and water, slightly so in ether. The platinum compound forms dark red prisms, soluble in water, alcohol, and ether (Malbot, Compt. rend 1887, **104**, 366). The nitrosamine, $(C_4H_9)_2N\ NO$, is a disagreeably smelling oil; m.p. 0°; b p. 213°–216° (with decomposition); obtained by the action of potassium nitrite upon the hydrochloride (Ladenburg, Ber. 1879, **12**, 949).

(*c*) *Di-tertiary butylamine*,

$$[(CH_3)_3C]_2NH;$$

produced as iodide when tertiary butyl iodide and tertiary butylamine are heated to 50°; at 70° the mixture is decomposed, forming *iso*butylene and tertiary butylammonium iodide (Rudnew). The iodide is easily soluble in water or alcohol; the aqueous solution evolves tertiary butylamine on heating.

3. **Tributylamines.**

(*a*) *Tri-normal butylamine*, $(C_4H_9)_3N$; b p. 211°–215° at 740 mm.; sp.gr. 0 791 at 0°, 0 7782 at 20°, 0·7677 at 40°. From butyl cyanate and potash, together with the mono- and di- compounds. With butyl iodide it forms tetrabutyl ammonium iodide, $N(C_4H_9)_4I$, which crystallises in small plates (Lieben and Rossi, Annalen, 1873, **165**, 115) Also formed by the action of ammonia on butyl chloride; b p. 216 5° (Berg, Ann Chim. Phys. 1894, [vii], **3**, 299).

(*b*) *Tri-iso butylamine* $(C_4H_9)_3N$; b p. 177°–180° (Reimer, Ber. 1870, **3**, 757); 184°–186° (Sachtleben, Ber. 1878, **11**, 733). Sp gr. 0 785 at 21° (S.). From di*iso*butylamine and *iso*butyl bromide (R.). From the alcohol and ammoniacal zinc chloride at 270° (Merz and Gasiorowski, Ber. 1884, **17**, 627); also from *iso*butyl iodide and aqueous ammonia at 160° (Malbot, Compt. rend. 1887, **105**, 574). Is not miscible with water. Forms salts with hydrochloric, nitric, and sulphuric acids, which are extremely soluble and crystallise with difficulty. The platinichloride forms large ruby-red crystals (Malbot, Compt. rend. 1887, **104**, 366).

Tributyl Phosphine. Tri-*n*-butyl phosphine, b.p. 149°–150°/50 mm. has been prepared by the action of phosphorus trichloride on butyl magnesium bromide (Davies and Jones, J.C.S. 1929, **133**, 1262).

Butylenes.

Three isomeric butylenes are possible and all are known.

Many methods of obtaining them by catalytic dehydration of the alcohols have been described Brown and Reid (J. Physical Chem. 1924, **28**, 1077) obtained the best yield using a mixture of alumina and blue oxide of tungsten, while Lazier and Adkins (J. Amer. Chem. Soc. 1925, **47**, 1719; 1926, **48**, 1671) prefer a mixture of alumina

and zinc oxide. Matignon, Moureu, and Dodé (Bull. Soc. chim. 1935, [v], 2, 1169) have shown that butyl alcohol when dehydrated with highly pure alumina yields α-butene, while if a trace of impurity is present the β-isomeride is produced.

Mailhe has shown (1932, A, 250) that when butylenes are passed over silica heated to 650°–700° a mixture of liquid unsaturated and aromatic hydrocarbons is produced. The ozonolysis in methyl chloride at −90° has been investigated by Briner and Meier (Helv. Chim. Acta, 1929, **12**, 529).

1. *Normal* (α)*-butylene. Ethyl ethylene,*

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2;$$

b.p. −5°.

Formation.—From normal butyl iodide and alcoholic potash (Saytzeff, J. pr. Chem. 1871, [ii], **3**, 88; Grabowsky and Saytzeff, Annalen, 1875, **179**, 330). From bromethylene and zinc-ethyl (Wurtz, Annalen, 1867, **152**, 21), together with butyl alcohol. From normal butylamine and nitrous acid (V. Meyer, Ber. 1877, **10**, 136). Prepared by digesting on the water-bath 100 g. normal butyl iodide, 200 g. potash, and 150 g. alcohol (90%) (S.). Coffin and Maass (J. Amer. Chem. Soc. 1928, **50**, 1427) have made a comparison of the physical properties of the gas prepared in this way and that prepared following the method of King (J.C.S. 1919, **115**, 1404) using butyl alcohol and phosphoric acid. It has also been prepared from allyl bromide and magnesium methyl bromide (Lucas and Dillon, J. Amer. Chem. Soc. 1928, **50**, 1460).

α-Butylene is a gas at ordinary temperatures, which combines readily with hydriodic acid to form secondary butyl iodide; and with hypochlorous acid to form chloromethylethyl carbinol, $EtCH(OH)CH_2Cl$. Passed over copper heated to redness forms butadiene, $CH_2{:}CH{\cdot}CH{:}CH_2$, which may be polymerised to rubber by means of metallic sodium (B.P. 9722, 1911). It is sparingly soluble in concentrated sulphuric acid.

2. β*-Butylene. Symmetrical dimethylethylene,* $CH_3{\cdot}CH{:}CH{\cdot}CH_3$; b.p. 1° at 741·4 mm. (Lieben, Annalen, 1869, **150**, 108); sp.gr. 0·635 at −13·50 (Puchot, Bull. Soc. chim. 1878, [ii], **30**, 188). Formed by the action of potash upon secondary butyl iodide (Luynes, Annalen, 1864, **129**, 200; Lieben). Together with *iso*butylene by dropping *iso-* or normal butyl alcohol upon strongly heated zinc chloride (Nevolé, Bull. Soc. chim. 1875, [ii], **24**, 122; Le Bel and Greene, Amer. Chem. J. 1880–1881, **2** 23). From trithioaldehyde$(C_2H_4S)_3$ and copper (Eltekow, Ber. 1877, **10**, 1904). By heating a mixture of methyl iodide and allyl iodide with sodium (Wurtz, Annalen, 1867, **144**, 235).

Preparation.—*iso*Butyl alcohol is allowed to drop upon heated zinc chloride, and the evolved gas is led into sulphuric acid diluted with half its volume of water; this retains the *iso*butylene. The unabsorbed gas is led into bromine, and is again liberated by action of sodium (Le Bel and Greene, Bull. Soc. chim. 1878, [2], 29, 306). More recently Read and Prisley (J. Amer. Chem. Soc. 1924, **46**, 1512) have prepared it by the following series of reactions: *iso*butyl alcohol (1 kg.) is passed over a catalyst of lump pumice and alumina heated in a glass tube to 450°–475°. The issuing gas is absorbed in kerosene and rehydrated with 50% sulphuric acid when 550–580 g. trimethyl carbinol are obtained. This is then dehydrated in a similar way and yields 225–250 g. of almost pure β-butylene. Two stereoisomeric modifications from tiglic and angelic acids respectively have been described (Wislicenus, Annalen, 1900, **313**, 228).

β-Butylene combines with bromine to form a dibromide boiling at 156°–158°. This compound, by the action of potash, forms monobromopseudobutylene, $CH_3{\cdot}CBr{:}CH{\cdot}CH_3$; b.p. 87°–88° (Hölz, Annalen, 1889, **250**, 230). Chlorine forms a dichloride; b.p. 112°–114° (Chechoukow (Scheschukoff), Bull. Soc. chim. 1885, [ii], **43**, 127).

3. γ*-Butylene.* iso*Butylene, unsymmetrical dimethylethylene,* $(CH_3)_2C{:}CH_2$; b.p. −6° (Butlerow, Z. Chem. 1870, 236); m.p. −146·8°; b.p. −6·6° (Coffin and Maass, Trans. Roy. Soc. Can. 1927, [iii], **21**, III, 33). Liquefied by a pressure of 2–2½ atmospheres at 15°–18°. Is produced by the dry distillation of fats (Faraday, Phil. Trans. 1825, **115**, 440); by heating the vapour of fusel oil to redness (Wurtz, Annalen, 1857, **104**, 249), together with ethylene and ethane; also from light petroleum, "ligroin" (b.p. 60°–90°) (Prunier, Jahresber. 1873, 347); from *iso-* or *tert*-butyl iodide and alcoholic potash (Butlerow, Annalen, 1867, **144**, 19); by heating trimethyl carbinol and dilute sulphuric acid (1 vol. H_2SO_4 to 2 vols. water) (Butlerow); from *iso*butyl alcohol and zinc chloride though in very small quantity (Nevolé, Bull. Soc. chim. 1875, [ii], **24**, 122).

Preparation.—(1) 5 parts of *iso*butyl alcohol, 5 parts sulphuric acid, 1 part of water and sand are heated together (Lermoutow, Annalen, 1879, **196**, 117). (2) Puchot's method (Ann. Chim. Phys. 1883, [5], **28**, 508) of heating *iso*butyl alcohol with a mixture of sulphuric acid, potassium sulphate, and gypsum gives a mixture of pseudo- and *iso*butylene. (3) A mixture of 2 parts of caustic potash and 3 parts of alcohol (90%) is slowly added to 2 parts of *iso*butyl iodide and gently warmed (Butlerow, Z. Chem. 1870, 238). Butylene is a gas, with unpleasant smell, slightly soluble in water and readily soluble in sulphuric acid; combines with hydriodic acid to form *tert*-butyl iodide. A mixture of three parts of sulphuric acid and 1 part of water completely absorbs the gas; on distilling the diluted solution trimethyl carbinol is evolved. It forms a mercury compound, $C_4H_8(HgNO_3)(Hg_2NO_3)$, (Denigès, Compt. rend. 1898, **126**, 1043). Oxidising agents—*e.g.* potassium permanganate—form carbon dioxide, formic and acetic acids, and oxalic acid (and in the case of chromium trioxide, acetone) (Zeidler, Annalen, 1879, **197**, 251). By the action of a mixture of 5 parts sulphuric acid and 1 part of water forms dodecylene (tri*iso*butylene), $C_{12}H_{24}$; b.p. 177·5°–178·5°; sp.gr. 0·774 at 0° (Butlerow, Ber. 1873, **6**, 561).

Butylene Alcohol *v. Butylene glycols.*

Butylene Dibromides.

1. *Normal butylene dibromide, $\alpha\beta$-dibrombutane,*

$CH_3 \cdot CH_2 \cdot CHBr \cdot CH_2Br$; b.p. 165 6°–166°; sp.gr. 1·876 at 0° (Wurtz, Annalen, 1869, **152**, 23), 1·8503 at 0°, 1·8204 at 20°/0° (Grabowsky and Saytzeff, Annalen, 1875, **179**, 332). Formed from α-butylene and bromine (Wurtz); from normal butyl bromide and bromine at 150° (Linnemann, Annalen, 1872, **161**, 199). Gives α-butylene by action of sodium.

2. *β-Butylene dibromide, βγ-dibrombutane,* $CH_3 \cdot CHBr \cdot CHBr \cdot CH_3$; b p. 158°; sp gr. 1·821 at 0°. Formed from β-butylene and bromine (Wurtz, Annalen, 1867, **144**, 236), or by heating α- or β brombutane with iron and bromine (V. Meyer and Muller, J. pr. Chem. 1892, [ii], **46**, *180). Decomposed by heating to 140°* with water and lead oxide forming lead bromide and methyl ethyl ketone (Eltekow, Chem. Soc. Abstr. 1879, *34*).

3. iso*Butylene dibromide, αβ-dibrom-β-methyl propane,* $(CH_3)_2CBr \cdot CH_2Br$; b.p. 148°–149° at 737 mm.; sp gr. 1·798 at 14° (Linnemann, Annalen, 1872, **162**, 36), b.p. 149 6° (corr.) (Thorpe), sp.gr. 1·7434 15°/15° (Perkin). From *iso*butylene and bromine (L.; also Wurtz, Annalen, 1857, **104**, 249; Hell and Rothberg, Ber. 1889, **22**, 1737). By heating with water to 150° *iso*butyraldehyde and *iso*butylene glycol are formed.

4. *Tetramethylenedibromide, αδ dibrombutane,* $CH_2Br \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot Br$, boils at 188°–190° (Gustavson and Demjanoff, J. pr. Chem. 1889, [2], **39**, 543). (*See also* Hamscourt, Compt. rend. 1901, **132**, 345).

5. *ββ-Dibrombutane,* $CH_3 \cdot CBr_2 \cdot CH_2\,CH_3$; boils at 144°–145° (Holz, Annalen, 1889, **250**, 232).

6. *αγ-Dibrombutane,*

$$CH_2Br\;CH_2 \cdot CH_2Br\;CH_3;$$

boils at 174°–175° (Perkin, J.C.S. 1894, **65**, 963).

Butylene Cyanide.

iso*Butylene dicyanide* (*dimethyl succinonitrile*), $CN\;C(CH_3)_2 \cdot CH_2 \cdot CN$; b p. 218°–220°, prepared by treating an aqueous alcoholic solution of potassium cyanide with γ butylene bromide, and allowing the mixture to stand for a fortnight. A colourless oil, moderately soluble in water *Heated to 150° with strong hydrochloric acid, it* is decomposed into ammonia and dimethyl succinic acid (Hell and Rothberg, Ber. 1889, **22**, 1737).

Butylene Glycolchlorhydrin, β-chloro-*iso*butylalcohol, $(CH_3)_2\,CCl\;CH_2 \cdot OH$. From *isobutylene and hypochlorous acid (Butlerow,* Annalen, 1867, **144**, 25). Soluble in large excess of water. *See also* Michael and Leighton (Ber. 1906, **39**, 2157).

β-Chloro*iso*butyl alcohol is also formed by the union of hydrogen chloride with *iso*butylene oxide, which results from the action of dry powdered potassium hydroxide on chloro trimethyl carbinol. The last may be prepared from magnesium methyl bromide, chloroacetone or ethyl chloroacetate. β-chloro*iso*butyl alcohol boils at 132°–133°. It forms a nitrate by the action of concentrated sulphuric and nitric acids, $C(Me)_2Cl \cdot CH_2O \cdot NO_2$, and a nitrite, $C(Me)_2Cl\;CH_2O \cdot NO$, with nitrous acid, which distinguishes it from the isomeric chlorotrimethyl carbinol (L. Henry, Compt. rend. 1906, **142**, 493).

The *bromohydrin*, b.p. 56°–58°/11 mm., has been prepared by De Montmollin and Matile (Helv. Chim. Acta, 1924, **7**, 106).

Butylene Diamines.

General methods of preparation and characterisation have recently been described by Strack and Fanselow (Z. physiol. Chem. 1929, **180**, 153).

1. *Tetramethylenediamine* (*putrescine*), αδ-diaminobutane,

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2,$$

occurs in urine and fæces in cases of cystinuria, and also arises during the putrefaction of herrings. It is prepared by reducing an alcoholic *solution of dicyanoethylene with sodium* (Ladenburg, Ber. 1886, **19**, 780; Lellmann and Wurthner, Annalen, 1885, **228**, 229); or in a similar manner from succinaldehyde dioxime (Ciamician and Zanetti, Ber. 1889, *22*, 1968, 1970). Colourless crystals melting at 27°–28° (C.Z.) and boiling at 158°–160°. Smells like piperidine. It is strongly basic, readily absorbs CO_2, and forms a well-defined dihydrochloride, aurichloride and platinichloride. The picrolonate is of some physiological importance (Otori, Chem. Soc. Abstr. 1905, ii, 126).

Willstätter and Heubner have prepared the tetramethyl derivative of tetramethylene diamine, and the biquaternary hexamethylammonium salt corresponding to it (Ber. 1907, **40**, 3871, 3874).

2. *Dimethylethylenediamine, βγ-diaminobutane,* $CH_3 \cdot CHNH_2 \cdot CHNH_2 \cdot CH_3$, has been prepared by Angeli (Ber. 1890, **23**, 1358).

*Iso-*Butylacetic Acid *v.* Caproic Acid.

Butyl Chloral *v.* Chloral.

Butyl-lactinic Acid *v.* Hydroxybutyric Acids.

Butylene glycols.

1. *Normal-α butylene glycol, αβ-dihydroxybutane,* $CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$; b.p. 191°–192° at 747·1 mm.; sp gr. 1·0189 at 0°/0°, 1 0059 at 17·5°/0°; from normal butylene dibromide (Saytzeff and Grabowsky, Annalen, 1875, **179**, 332). The diacetate, b p. 196°–199°, has been prepared from the bromide and potassium acetate (De Montmollin and Matile, *l c.*).

2. *Normal β-butylene glycol, αγ dihydroxybutane,* $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2OH$; b.p. 203 5°–204° (Kekulé, Annalen, 1872, **162**, 310); sp gr. 1·0259 (*Wurtz, Jahresber. 1873, 474;* Bull. Soc. chim. 1884, [ii], **41**, 362). Produced in small quantity by the reduction of dilute aqueous solution of aldehyde by sodium-amalgam (K.). Prepared from β-oxybutyric aldehyde by reduction with sodium amalgam (W.).

3. *Symmetrical dimethylethylene glycol, βγ-dihydroxybutane,* $CH_3 \cdot CH(OH)CH(OH)CH_3$; b p. 183°–184°. Formed by heating for 6 or 7 hours 1 vol. of symmetrical dimethylethylene oxide, C_4H_8O, with 3 vols. of water to 100° (Eltekow, Chem. Soc. Abstr. 1883, **44**, 566).

4. *Tetramethylene glycol, αδ dihydroxybutane,* $OH \cdot (CH_2)_4 \cdot OH$; boils at 235° (Boeseken, Rec. trav. chim. 1915, **34**, 100).

5. A *butylene glycol*, differing from the above,

boiling at 183°–184°; has also been prepared by Wurtz (Ann. Chim. Phys. 1859, [iii], 55, 452); sp.gr. 1·048 at 0°.

6. iso*Butylene glycol, αβ-dihydroxy-α-methylpropane*, $(CH_3)_2C(OH)CH_2\cdot OH$; b.p. 176°–178°; sp.gr. 1·0129 at 0°, 1·003 at 20°. Produced by the fermentation of sugar in presence of tartaric acid (Henninger and Sanson, Compt. rend. 1888, **106**, 208). Formed by heating *iso*butylene bromide with potassium carbonate and water (Nevolé, Bull. Soc. chim. 1877, [2], **27**, 63); also by oxidation of *iso*butylene by means of potassium permanganate in neutral aqueous solution (Wagner, Ber. 1888, **21**, 1232).

7. *α-Methyl propanediol*,

$$OH\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot OH,$$

b.p. 214°–214·5°/771 mm. (Faworski, Annalen, 1907, **354**, 356).

Butylene Diiodide, *αγ-diiodobutane*,

$$CH_3\cdot CHI\cdot CH_2\cdot CH_2I;$$

sp.gr. 2·291. From *β*-butylene glycol and hydriodic acid (Wurtz, Compt. rend. 1883, **97**, 473).

*iso***Butylene Dinitrite,** $C_4H_8(NO_2)_2$. By treatment of *iso*butylene with concentrated nitric acid (Haitinger, Monatsh. 1881, **2**, 287). Forms a crystalline mass. Probably the same body was obtained by Beilstein and Kurbatow (Ber. 1881, **14**, 1621) by treating the petroleum of Tiflis (b.p. 40°–50°) with nitric acid (sp.gr. 1·52). It formed needles which melted at 96°. They were insoluble in water but soluble in alcohol and ether.

Butylene Oxides. C_4H_8O.

1. n-*Butylene oxide*, $CH_3\cdot CH_2\cdot \overset{\diagup O}{CH}\text{—}\ CH,$ b.p. 58·5°–59°, has been prepared from the bromohydrin and alkali (De Montmollin and Matile, Helv. Chim. Acta, 1924, **7**, 106).

2. iso*Butylene oxide*, $(CH_3)_2C\text{——}CH_2$ (with O bridging); b.p. 51°–52°; sp.gr. 0·8311 at 0°. From the chlorhydrin, C_4H_9OCl, and potash (Eltekow, J.C.S. 1883, **44**, 566).

3. *s-Dimethylethylene oxide*,

$$CH_3\cdot \overset{\diagup O \diagdown}{CH\cdot CH}\cdot CH_3;$$

b.p. 56°–57°; sp.gr. 0·8344 at 0°. Formed from the chlorhydrin (prepared from the symmetrical dimethylethylene and hypochlorous acid) and potash (Eltekow, *l.c.*). E. G. N.

*iso, sec-, tert-***BUTYL CARBINOL** *v.* AMYL.

BUTYL CARBITOL. Mono-*n*-butyl ether of diethylene glycol. Wetting out agent.

BUTYL CELLOSOLVE. Mono-*n*-butyl ether of ethylene glycol. Nitrocellulose solvent and wetting out agent.

BUTYLCHLORAL HYDRATE, crotonchloral hydrate, *ααβ-trichlorobutylidene glycol*,

$$CH_3\cdot CHCl\cdot CCl_2\cdot CH(OH)_2,$$

m.p. 78°. Sedative. Hypnotic.

BUTYN, *γ*-di-*n*-butylaminopropyl *p*-aminobenzoate, local anæsthetic. (Abbott, Chicago; Pharmaceutical Products, London.) B.P.C.

BUTYRIC ACIDS, $C_3H_7\cdot COOH$.

Normal Butyric Acid,

$$CH_3\cdot CH_2\cdot CH_2\cdot COOH.$$

Occurrence.—In ordinary butter in combination with glycerol to the extent of about 3%; in the fruits of *Heracleum giganteum* and of *Pastinaca sativa* as hexyl butyrate and octyl butyrate respectively; also in the oil of *Eucalyptus Perriniana* as a *n*-butyl butyrate (Smith, J. Roy. Soc. New South Wales, 1914, **48**, 464). Butyric acid is also found in flesh juice, and is frequently a product of fermentation processes.

Preparation.—(1) Butyric acid is a frequent product of the oxidation of organic substances, such as albumen, fibrin, and casein—with manganese dioxide and sulphuric acid (Guckelberger, Annalen, 1847, **64**, 68).

(2) All amylaceous and saccharine substances that yield lactic acid on fermentation with *Bacillus acidi lactici* can undergo a further fermentation with *Bacillus butyricus* to yield *n*-butyric acid. This fact is made use of in the preparation of the acid.

Manufacture.—A 6–10% sugar solution is prepared from molasses or by mashing potato, maize or rice starch with malt; to this is added some nitrogenous nutrient medium (extract of malt or wheat, ammonium tartrate or phosphate), the solution is boiled and allowed to cool to the optimum temperature for fermentation by a vigorously growing bacterial culture which is added to it from a neighbouring vat. *B. butyricus* or a similar organism or a mixed culture is employed. Chalk is added to maintain neutrality during the fermentation, which goes on for about 9 days, while large volumes of H and CO_2 are evolved. The liquid is then filtered, concentrated, and the calcium butyrate which separates dried and distilled *in vacuo* with sulphuric acid, the distillate is purified by fractionation. Weizmann and Spiers in B.P. 164366, 3/6/18, claim a 13% yield of butyric acid from maize. Lefranc et Cie. in B.P. 186572, 2/2/22, describe the saccharification of wood (100 kg.) with subsequent fermentation to butyric acid (9–9·5 kg). On a laboratory scale, Heiduschka and Reymann (Pharm. Zentr. 1929, **70**, 87) fermented a 5% dextrose solution with an *Amylobacter* at 37° and obtained 56·3% of the theoretical yield of butyric acid.

(3) *n*-Butyric acid has been prepared by synthetical methods by Frankland and Duppa (Annalen, 1866, **138**, 218), and by Geuther and Frölich (*ibid.* 1880, **202**, 306). From *n*-butaldehyde by vapour-phase oxidation without and with a catalyst respectively (Carbide and Carbon Chemicals Corp., U.S.P. 1599737; Adam and Legg, B.P. 173004); with a colloidal solution of manganese butyrate as a catalyst (Comml. Solvents Corp., Canad. P. 249868).

Properties.—Butyric acid is a colourless liquid, having an odour resembling that of rancid butter, and a sour burning taste; m.p. −4·65° to −4·70° (English and Turner, J.C.S. 1915, **107**, 779); b.p. 162°; sp.gr. 0·9670 at 15°/15° and 0·9590 at 20°/4° (Perkin, J.C.S. 1884, **45**, 483); n_D^{20} 1·39906.

It is miscible with water, alcohol, and ether in all proportions, and from its aqueous solution

it can be separated by addition of calcium chloride. The acid is inflammable, and burns with a blue flame. Prolonged oxidation with nitric acid converts it into succinic acid. Among the products of electrolysis of potassium *n*-butyrate (F. Fichter and A. Bürgin, Helv. Chim. Acta, 1931, 14, 90) is *iso*propyl alcohol; the intermediate formation of dibutyryl peroxide $(Pr{\cdot}COO)_2$, decomposing to give propylene, which with butyric acid gives *iso*propyl butyrate, is postulated to account for this unusual reaction

Salts.—The metallic salts of *n*-butyric acid are generally soluble in water, and are crystalline. $Na\overline{B}$ and $K\overline{B}$ crystallise in indistinct nodules. $Ag\overline{B}$ crystallises in needles or monoclinic prisms, 100 parts of water at 14° dissolve 0·5 parts (Linneman and Zolta, Annalen, 1872, 161, 177, Grünzweig, Annalen, 1872, 162, 203). $Mg\overline{B}_2,5H_2O$ crystallises in very soluble scales (Pelouze and Gélis, Annalen, 1843, 47, 249). $Ba\overline{B}_2,4H_2O$ crystallises in nacreous scales, 1 part dissolving in 2·48 parts of water at 14° (Linneman and Zolta). $Ca\overline{B}_2,H_2O$ crystallises in rhombic prisms, 100 parts of water at 0° dissolve 19·4 parts (Hecht, Annalen, 1882, 213, 72), at 60°, 15·01 parts $Zn\overline{B}_2,2H_2O$ forms monoclinic prisms, 100 parts of water at 16° dissolve 10·7 parts of the crystallised salt (Grünzweig). $Cu\overline{B}_2,H_2O$ crystallises in triclinic forms (Alth, Annalen, 1854, 91, 176), and $Cu\overline{B}_2,2H_2O$ in monoclinic forms (Pelouze and Gélis).

Butyric acid occurs widely in wines and foodstuffs. Its estimation usually involves separation from acetic and propionic acids. Details for its estimation in wine are given by March and Portele (J C S 1890, 58, 1344): 500 c c. of the solution is distilled to a bulk of 125 c c., diluted to the original volume, and again distilled till only 125 c.c remains. This is repeated four times in all. The total acid in the distillate is estimated with baryta It is evaporated down, until it solidifies on cooling. The barium butyrate is then extracted with absolute alcohol (10 parts), and the aqueous solution of the separated salts treated with sulphuric acid and steam distilled, the acid in the distillate being subsequently titrated.

The detection and estimation of *n* butyric acid in foods is discussed by Grossfeld and Battay (Z. Unters. Lebensm 1931, 61, 129); and by Virtanen (Z. anal. Chem. 1928, 74, 321). The separation of formic, acetic, propionic and butyric acids is dealt with by Willcox (Chem. Soc. Proc. 1895, 202); Luck (Z. anal. Chem. 1870, 10, 185); Haberland (*ibid* 1899, 38, 217); Muspratt (J.S.C.I. 1900, 19, 204); Fyleman (J.S C.I. 1924, 43, 142T); Osburn and Werkmann (Ind Eng. Chem. (Anal.), 1931, 3, 264)

It can be determined colorimetrically by treating with cupric chloride and ammonium chloride, shaking with chloroform and comparing with standards. Acetic and formic acids do not interfere (Allgeier *et al*, J. Bact. 1929, 17, 79).

Butyryl Chloride is obtained by treating 96 parts of butyric acid with 100 parts phosphorus trichloride (Burcker, Ann. Chim. Phys. 1882, [v], 26, 468). B.p. 101°; sp gr. 1·0277 at 23°/4°.

Butyric Anhydride.—Prepared by the action of butyryl chloride on butyric acid (Linnemann, Annalen, 1872, 161, 179) or by the action of 1 mol. acetic anhydride on 2 mols. sodium butyrate (Michael, Ber. 1901, 34, 918). B p. 193°, $d^{12\cdot5}$ 0·978.

Butyramide. — Formed by heating dry ammonium butyrate (Hofmann, Ber. 1882, 15, 982). Prisms, m p. 115°, b p. 216°. Readily soluble in water.

a-Chlorobutyric Acid,

$$CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H,$$

is a thick liquid, soluble with difficulty in water (Markownikow, Annalen, 1870, 153, 241). B.p. 101°/15 mm.

β-Chlorobutyric Acid,

$$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H,$$

M p 16°, b p 98·5°–99·5°/12 mm. (Cloves, Annalen, 1901, 319, 360).

γ-Chlorobutyric Acid,

$$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

by treatment of γ butyrolactone with dry hydrogen chloride, m.p. 16°, b p. 115°–115·5°/13 mm. (Cloves, *l c.*).

a Bromobutyric Acid.—

$$CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H.$$

By brominating butyric acid in the presence of red phosphorus (Fischer, Ber. 1900, 33, 2387). Colourless oil B.p. 128°/25 mm. Moderately soluble in water.

β Bromobutyric Acid.—

$$CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2H.$$

By treating crotonic acid with hydrogen bromide (Brulé, Bull. Soc. chim. 1909, [iv], 5, 1019). M.p. 18°, b p. 122°/16 mm.

γ-Bromobutyric Acid.—

$$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

From γ-butyrolactone and hydrogen bromide at 100° (Henry, Compt. rend. 1886, 102, 369). M.p. 33°.

isoButyric Acid, $(CH_3)_2{\cdot}CH{\cdot}CO_2H$.

Occurrence.—*iso*Butyric acid occurs in the fruit of *Ceratonia Siliqua* (Grunzweig, Annalen, 1872, 162, 193), and in arnica root (*Arnica montana*) (Sigel, Annalen, 1873, 170, 348).

Preparation.—*iso*Butyric acid is most readily prepared by the oxidation of *iso*butyl alcohol with acidified potassium dichromate. Pierre and Puchot (Ann. Chim. Phys. 1873, [iv], 28, 366) give the following details: *iso*butyl alcohol (300 parts) is mixed with water (1,500 parts) and sulphuric acid (540 parts), and into the well cooled mixture finely powdered potassium dichromate (400 parts) is gradually introduced. An ethereal layer separates, consisting of *iso*butyl *iso*butyrate, which is saponified by excess alkali; the resulting salt being distilled with dilute sulphuric acid, and the aqueous acid purified by fractional distillation. Synthetical methods for preparing this acid have been described (Frankland and Duppa, Annalen, 1866, 138, 337; and Markownikow, Annalen, 1866, 138, 361).

Properties.—*iso*Butyric acid resembles its isomeride in appearance, but has a less disagreeable odour. It boils at 154·0° (corr.)

(Thorpe and Rodger, Phil. Trans. 1894, A, **185**, 486); sp.gr. 0·9651 at 0° and 0·9503 at 20°; n_D^{20} 1·39300 (Brühl, Annalen, 1879, **200**, 180). It dissolves in five times its volume of water.

*iso*Butyric acid has been detected among the products from the interaction of carbon monoxide and hydrogen at 370°–390°/400 atm. in presence of an alkali catalyst (Strada, Giorn. Chim. Ind. Applicata. 1934, **16**, 62).

Salts.—The metallic salts of *iso*butyric acid are more soluble in water than those of the normal acid. $Ag\overline{B}$ crystallises in prisms; 100 parts of water dissolve 0·93 part at 16° (Grünzweig, Annalen, 1872, **162**, 210). $Mg\overline{B}_2$ forms white scales. $Ca\overline{B}_2,5H_2O$ forms monoclinic crystals; 100 parts of water at 15° dissolve 36 parts (Grünzweig, *l.c.*). $Sr\overline{B}_2,5H_2O$; 100 parts of water at 17° dissolve 44 parts. $Ba\overline{B}_2,\frac{1}{2}H_2O$ forms monoclinic crystals (Fitz, Ber. 1880, **13**, 1316). $Zn\overline{B}_2,H_2O$—100 parts of water at 19° dissolve 17·3 parts (G.). $Pb\overline{B}_2$ crystallises in rhombs and dissolves in 11 parts of water at 16°.

iso*Butyryl chloride*, prepared by treating *iso*butyric acid with phosphorus trichloride and subsequently distilling (Reczei, Chem.-Ztg. 1928, **52**, 22); the use of silicon tetrachloride avoids the contamination of the acid chloride with S and P compounds (Montonna, J. Amer. Chem. Soc. 1927, **49**, 2114); boils at 92°; and has a sp.gr. 1·0174 at 20°/4° (Brühl, Annalen, 1880, **203**, 20).

iso*Butyric anhydride*, obtained by refluxing *iso*butyric acid with *iso*butyryl chloride for 12 hours, and subsequently fractionating the product. It boils at 181·5° at 734 mm., and has a sp.gr. 0·9574 at 16·5° (Tönnies and Staub, Ber. 1884, **17**, 850).

iso*Butyramide*, formed by heating ammonium *iso*butyrate; melts at 128°–129° (Hofmann, Ber. 1882, **15**, 982).

*a-Chloro*iso*butyric acid*,

$$(CH_3)_2CCl{\cdot}CO_2H,$$

melts at 31° and boils at 118° (Henry, Bull. Soc. chim. 1876, [ii], **26**, 24).

*a-Bromo*iso*butyric acid*,

$$(CH_3)_2CBr{\cdot}CO_2H,$$

prepared by treating *iso*butyric acid with bromine in the presence of red phosphorus (Volhard, Annalen, 1887, **242**, 161). M.p. 48°, b.p. 200°.

Butyric Esters.—These compounds are prepared in the laboratory by the action of butyric acid on the corresponding alcohols in the presence of some dehydrating agent such as sulphuric acid, the temperature being raised to complete the reaction. Commercially they can be made by vapour-phase esterification, the vapours of the acid and of an alcohol being passed over a catalyst, such as titanium oxide; with excess alcohol nearly theoretical yields are obtained (J. Usines Gaz. 1924, **48**, 17). Butyric esters are liquids which dissolve in alcohol and ether in all proportions, but are only sparingly soluble in water. Esters of *iso*butyric acid, especially with glycols, are used in perfumery and for flavouring (U.S.P. 1841430; Burger, Chem. Zentr. 1928, i, 2466).

Methyl n-*butyrate*, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2CH_3$, is a colourless liquid with a pleasant odour resembling that of pineapples. It boils at 102·3° at 760 mm. (Schumann, Pogg. Ann. 1881, [ii], **12**, 41), and has a sp.gr. 0·9194 at 0°/4°.

Ethyl n-*butyrate* resembles the methyl ester in odour, and is used in perfumery, and in confectionery under the name of pineapple oil. It boils at 119·9° at 760 mm. (Schumann, *l.c.*), and has a sp.gr. 0·8996 at 0°/4°.

n-*Propyl* n-*butyrate* boils at 142·7°/760 mm. (Schumann), and has a sp.gr. 0·8930 at 0°/4°.

iso*Propyl* n-*butyrate* boils at 129°, and has a sp.gr. 0·8787 at 0°/4°.

Butyl n-*butyrate* boils at 164·8° (corr.), and has a sp.gr. 0·8760 at 12° (Linnemann, Annalen, 1872, **161**, 195). A nitrocellulose solvent.

iso*Butyl* n-*butyrate* boils at 156·9° (Schumann), and has a sp.gr. 0·8798 at 0°.

iso*Amyl* n-*butyrate* boils at 178·6° (Schumann), and has a sp.gr. 0·8823 at 0°.

Hexyl and *octyl butyrates* occur in the oils from the fruits of *Heracleum giganteum* (Franchimont and Zincke, Ber. 1871, **4**, 824) and *Pastinaca sativa* (Renesse, Annalen, 1873, **166**, 80).

Esters of *iso*butyric acid have been prepared:

Methyl iso*butyrate* boils at 92·3°/760 mm. (Schumann), and has a sp.gr. 0·9112.

Ethyl iso*butyrate* boils at 110·1°/760 mm. (Schumann); its sp.gr. is 0·8903.

n-*Propyl* iso*butyrate* boils at 133·9°/760 mm. (Schumann); its sp.gr. is 0·8843.

iso*Propyl* iso*butyrate* boils at 118°–121°/727 mm., and has a sp.gr. 0·8787.

iso*Butyl* iso*butyrate* boils at 146·6°/760 mm. (Schumann); its sp.gr. is 0·8752.

iso*Amyl* iso*butyrate* boils at 168·8°/760 mm. (Schumann); and has a sp.gr. 0·8759 at 0°/4°.

BUTYRONE. Dipropyl ketone,

$$(C_3H_7)_2CO,$$

is prepared by distilling calcium butyrate or preferably a mixture of this with calcium carbonate (Schmidt, Ber. 1872, **5**, 597) or by passing butyric acid over any of the following catalysts: precipitated calcium carbonate at 450°–500° (Sabatier and Mailhe, Compt. rend. 1913, **156**, 1731), ferrous or ferric oxide at 430°–490° (Mailhe, Compt. rend. 1913, **157**, 220), cadmium oxide at 420°–430° (Mailhe, Bull. Soc. Chim. 1913 [4], **13**, 668) or manganic oxide at 400°–450° (Mailhe, Compt. rend. 1914, **158**, 832). It is a liquid of b.p. 144°–145° and d_4^{20} 0·8217, and is used as a solvent for nitrocellulose. It is oxidised by chromic acid to a mixture of propionic and butyric acids, and is reduced by sodium amalgam to a secondary alcohol, $C_7H_{16}O$, and butyrone-pinacone, $C_{14}H_{30}O_2$ (Kurtz, Annalen, 1872, **161**, 205).

An isomeride, *di-isopropylketone*, b.p. 124°–126°, d^{17} 0·8254, can be prepared by distilling calcium *iso*butyrate (Münch, Annalen, 1876, **180**, 327). Neither butyrone nor its isomeride forms a bisulphite compound.

γ-BUTYROBETAINE *v.* Betaines.

γ-BUTYROLACTONE. The lactone of γ-hydroxybutyric acid.

BUXINE is an amorphous alkaloid discovered by Fauré (J. de Pharm. 1830, [ii], **16**,

432) in the bark of *Buxus sempervirens* L. the box tree, which has been used in intermittent fever. Walz (Neues Jahrb. Pharm. 1860, 12, 302) declared it to be identical with bebeerine (from *Nectandra Rodioei* Hook, or greenheart), which latter alkaloid was for a time known as buxine, until the identity was disproved by Scholtz (Arch. Pharm. 1898, 236, 530). In addition to buxine, Barbaglia (Gazz. chim. ital. 1883, 13, 249) found two other amorphous and one crystalline alkaloid in box leaves, and Martin-Sans (Compt. rend. 1930, 191, 625) has demonstrated the occurrence of alkaloids in other *Buxaceæ* by microchemical methods. G. B.

BYSSUS, or silk of oyster, is the secretion of a gland of certain mussels, which in the air sets into silk-like threads. It is stated in the past it has been woven into textiles (Abderhalden, Z. physiol. Chem. 1908, 55, 236). The chemical and X-ray investigation of byssus (in its natural state, and stretched) shows that it consists of a mixture of chains of complex (keratin type) and chains of simple (silk fibroin type) amino acids. It is the only natural fibre in which the molecules have no orientation, and this accounts for its physical properties (Centola, Gazzetta, 1936, 66, 71).

BYTOWNITE or **LABRADORITE** *v.* BASALT.

C

CAAPI. *Ayahasco.* The root of the Bolivian vine *Banisteria caapi*, contains three alkaloids and yields a stimulating beverage.

CABALONGA DE TABASCO. A Mexican drug. The seeds of *Strychnos triplinervia*, contain 1·83% of strychnine and brucine.

CABARDINE MUSK. An inferior variety of genuine musk from Siberia and North China.

CABBAGE. *Brassica oleracea.* Many varieties of this leafy vegetable have been developed by the horticulturalist for domestic purposes and for cattle feeding. The customary classification based on the structure of the plants includes:

(i) Ordinary cabbage (var. *capitata*), forming a compact head of leaves, the internal ones being blanched. With this type may be included for convenience the Chinese cabbage or celery cabbage, *B. pekinensis* or *B. pe tsai* Bailey, which also forms a compact head but is more elongated in shape than the customary European varieties. *B. chinensis*, also referred to as "Chinese cabbage," is not apparently a "heading" variety.

(ii) Kale (var. *acephala* D.C.) includes a number of types of branching habit in which the tendency to form compact heads is absent. In most forms the stems become woody as in the ordinary cabbage. In a few cases (*e.g.* marrow-stemmed kales) the stems remain sufficiently succulent, even in mature plants, to be readily consumed by cattle and sheep.

(iii) Broccoli and cauliflower (var. *botrytis* D.C.) are characterised by a restricted leaf development and the production of a compact head of imperfect flowers, which form the edible portion.

(iv) Brussels sprouts (*q.v.*) (var. *gemmifera*), in which numerous small compact "cabbage" heads develop in leaf axils on a tall, thick mainstem.

(v) Kohl-rabi (var. *Caule-Rapa*), the stem of which thickens (above ground) to produce a round turnip-like growth (the edible portion) from the surface of which a few leaves develop.

All cabbage varieties show a general similarity of composition. The following are typical analyses expressed as percentage of fresh weight:

	Water.	Crude protein.	True protein.	Fat.	N-free extract.	Fibre.	Ash.
Ordinary cabbage [1] . .	84·7	2·5	—	0·7	8·1	2·4	1·6
Ordinary cabbage [2] . .	91·5	1·6	—	0·3	4·5	1·1	1·0
Ordinary cabbage [3] . .	92·1	2·0	1·23	0·18	4·03	0·82	0·75
Chinese cabbage . .	96·0	1·58	—	0·05	1·61	0·5	0·66
Red cabbage	93·1	1·50	0·88	0·5	3·79	0·8	0·66
Kale . . .	91·2	2·82	—	0·20	2·94	1·05	1·74
Broccoli (flower) .	88·1	4·4	—	0·74	—	1·42	1·69
Cauliflower .	90·7	3·11	1·70	0·40	3·73	1·15	0·93
Kohl rabi [4] .	92·8	2·02	1·03	0·14	3·57	0·64	0·86

[1] Whole heads [2] Edible portion.
[3] Savoy cabbage. [4] Edible portion.

The nitrogen content of cabbage varies considerably according to growth conditions and manurial treatment (A. W. Blair, New Jersey Agric. Exp. Sta. Bull. 1934, No. 571), but in all cases includes a large proportion of non-protein nitrogen. Yoshimura (Z. Unters. Nahr.-Genussm. 1910, 32, 253) reports less than 30% of the total nitrogen as protein and a considerable proportion of nitrogen bases, *e.g.* arginine, lysine, and choline together with small amounts of histidine and betaine. Tryptophane, and also the enzyme erepsin which produces tryptophane from more complex bodies, is also recorded (Blood, J. Biol. Chem. 1910, 8, 215).

From the ether extract of cabbage, Ozaki (J. Agric. Chem. Soc. Japan, 1930, 6, 688) isolated a dark-coloured oil having saponification value 144·1, iodine value 103·4, Reichert-Meissl value 2·0, acid value 21·2, and unsaponifiable matter 21·7%. The saturated acids from the oil comprise principally palmitic together with arachidic and small amounts of myristic but no stearic acid. Unsaturated acids consist largely of an isomeride of linolic acid, linolenic and an isomeride of oleic acid. A waxy substance isolated from blanched leaves yielded palmitone and *n* hentriacontane. Chibnall and Channon (Biochem. J. 1927, 21, 225, 233, 479, 1112; 1929, 23, 168–176) in an examina-

tion of the ether-soluble constituents of the expressed juice of leaves report the following constituents (as percentage of the extract):

α- and β-chlorophyll	9·3
Carotene	0·5
Xanthophyll	0·8
Calcium phosphatidate	18·5
Other Ca salts (unidentified)	5·1
Fe compounds (unidentified)	3·0
Glycerides and waxes	17·4
Glycerol	1·4
Unsaponifiable fraction	12·3
Sterols	4·4
Unidentified alcohols and hydrocarbons	13·3

The fatty acids of the fats and waxes included palmitic, stearic, linolic, and linolenic acids. *n*-Nonacosane and di-*n*-tetradecyl ketone were the principal constituents of the unsaponifiable matter.

Among the carbohydrate constituents of the cabbage family sugars are present, if at all, in very small amounts. The highest recorded proportions occur in ordinary cabbage in which Peterson *et al.* (Canner, 1935, **61**, 19) report 3–4%. Dextrose and lævulose are found in small amounts in cauliflower (Dmochowski and Tollens, J. Landw. 1910, **58**, 27) in which mannite was also detected by Busolt (*ibid.* 1913, **61**, 153). Buston and Schryner isolated a crystalline carbohydrate, probably

$$CH_2(OH)CH(OH)O{\cdot}CH_2{\cdot}OH$$

(Biochem. J. 1923, **17**, 470) which is possibly concerned in pyrone ring formation during the synthesis of anthocyanin pigment. The pentosan content is also small, recorded values being 2·03% in kale, 0·91% in broccoli flowers, and 1·37% in kohl-rabi (Wittmann, Z. landw. Verswes. Öst. 1901, **4**, 131; Nelson and Mottern, J. Amer. Chem. Soc. 1931, **53**, 1909). The last-named authors also record 1·3% of starch in broccoli.

The pigment of red cabbage has been isolated by H. Willstaedt (Biochem. Z. 1931, **242**, 303; 1935, **276**, 262) and also by Chmielewska (Rocz. Chem. 1933, **13**, 725), and is characterised as an anthocyanin chloride, $C_{28}H_{33}O_{16}Cl$, isomeric with peonin. T. Milobedski and W. Szczypiński (Rocz. Chem. 1934, **14**, 1088) also describe a pigment rubrobrassicin from which elimination of sinapic acid yields an indicator suitable for acidimetry in the presence of carbon dioxide.

Cabbages are rich in vitamin-*C*, a recent evaluation by N. Yarusova (Z. Unters. Lebensm., 1935, **69**, 375) showing 270–322 units per kg. From 20 to 70% of this may pass into the water in which the vegetable is cooked. According to S. Gould *et al.* (Food Res. 1936, **1**, 427) the vitamin-*C* content of early summer cabbage is greater than that of autumn varieties. After cutting there is a steady decrease in the proportion of vitamin-*C*, loss of which is greater in cold storage than at ordinary temperatures.

The mineral contents of the cabbage family vary considerably with growth conditions but show a general similarity of order. The following data from various sources are typical, and are expressed as percentage of the dry matter:

	Cabbage.	Kale.	Kohl-rabi.	Cauli-flower.	Broc-coli.
K	3·9–4·3	—	—	2·9	1·86
Ca	0·67–0·78[1]	0·96	0·07	0·32	0·33
Mg	0·30–0·35	—	—	0·19	0·13
Fe	0·009–0·014	0·17	—	0·014	0·06
Mn	0·004–0·0018	—	—	0·025	0·033
P	0·46	0·30	—	0·71	0·57
S	0·53–0·62	—	—	—	—
Cl	0·26–0·63	—	—	0·3	—
Al	0·2–0·008[2]	—	—	—	—
Cu	0·0006	—	0·0014	0·002	—
Zn	0·0012–0·0017	—	—	0·002	—

[1] Outer leaves of cabbage contain 20–30 times as much calcium as inner leaves (S. J. Cowell, Biochem. J. 1932, **26**, 1422).

[2] Analyses (J. Bertrand and Lévy, Bull. Soc. Sci. Hyg. Aliment. 1931, **19**, 359) show that the aluminium in cabbage is almost entirely contained in the outer green leaves.

Sauerkraut is obtained by submitting the cabbage to a lactic type of fermentation, *Streptococcus lactis* and *Leuconostoc mesenteroides* being the dominant organisms concerned. Lactic acid with smaller proportions of acetic and propionic acids are produced, and in good quality kraut proteolysis is limited. Quality is largely influenced by the nature of the "starter" cultures used. Peterson, Fred and Viljoen (Canner, 1925, **61**, 19) give the following analysis ranges for sauerkraut.

Water.	Non-volatile acids, as lactic.	Volatile acid, as acetic.	Sugars.
89·6–91·5	1·13–1·52	0·28–0·42	0·09–0·77

A considerable proportion of the vitamin-*C* of the cabbage is retained in sauerkraut.

A. G. Po.

CACAO (COCOA) BUTTER is the fat present in the "beans" or seeds of the cacao *Theobroma cacao* L. and certain closely allied species and their hybrids (Fam. Sterculiaceæ). According to van Humboldt, the cacao tree appears to have originated in the forests of the Amazon and Orinoco (Ecuador, Colombia, and Venezuela), but it has been extensively cultivated from very early times in other tropical countries, Central America, Brazil, and the West Indies, and more recently in West Africa (particularly the Gold Coast and Nigeria) and Ceylon (*see* Cocoa).

The bulk of commercial cacao butter is obtained by the expression of the fermented and roasted cacao nibs, *i.e.* cotyledons, in the course of the manufacture of cacao (cocoa) powder: correspondingly the commercial production of the fat (and of eating chocolate, in the manufacture of which it is used) dates from the introduction of a partly defatted cocoa powder by Van Houten in 1828, although the art of pressing out a little of the fat from the bean appears to have been known at least 140 years before (A. W. Knapp, "Cocoa and Chocolate Industry," J. Pitman & Sons, London, 1930, p. 25). It may be noted, however, that the fermentation and roasting processes to which the bean is subjected do not appreciably affect the physical and chemical properties (apart from the aroma and colour) of the fat (*cf.* Heiduschka and Herb, Pharm. Zentr. 1908, **49**, 375; Strube, Z. öffentl. Chem. 1908, **14**, 67; Fincke, Z. angew. Chem. 1925, **38**, 699; Z. Unters. Lebensm. 1928,

56, 326; "Kakaobutter u. ihre Verfälschungen," Stuttgart, 1929, pp 168–174); there is also little difference in the characters of fats from beans of different geographical origin or botanical variety (*cf.* Davies and McLellan, J.S.C.I. 1904, 23, 480).

The shell (testa) and germ (radicle) of the cacao seed also contain a small amount of fat, which can be recovered by extraction with solvents: these fats, however, are of no great importance and will be considered separately (*v. infra*) as they are, in general, unsuitable for edible use, and are excluded from use in chocolate products under the terms of the resolution adopted by the International Congress of Chocolate and Cacao Manufacturers in Antwerp, 1930. This defines the term "cacao butter" (for chocolate manufacture) as "the fat obtained by mechanical means (*i.e.* by expression) from cacao mass (solubilised or not)" which is derived from cacao nib containing not more than 5% of shells and germs (calculated on a dry fat free basis, *i.e.* equivalent to not more than about 2% on the nib as prepared). Similar definitions have been adopted for purposes of Food Legislation in many foreign industrial countries. It may be noted that in Germany (*cf.* Verordnung über Kakao u.s.w. 15/7/33) the term "*Kakaobutter*" may only be applied to such an expressed fat: refined or extracted fat from cacao beans is designated as "*Kakaofett*."

The expression of cacao butter is a necessary stage in the manufacture of cocoa powder, which may be outlined as follows (for further details, *see* COCOA, CHOCOLATE): The dry fermented cacao beans (seeds), which contain about 47% of fat, are first cleaned to remove adherent dirt, etc., and then are roasted in rotating drums over coke or gas fires, in order to develop the typical chocolate flavour and to loosen the shells or husks from the kernels. The cooled, roasted beans are then kibbled, *i.e.* passed between rollers which are adjusted so as to crack the shells without crushing more than a small proportion of the kernels, after which the tiny rod-like germs (*i.e.* radicles) are removed by sifting, and the broken shells by winnowing; a further sifting and grading process removes any fine fragments of kernel, shell, etc. (which are worked up separately for fat, cattle-food, etc.) from the main product, which consists of clean, almost shell-free nib (cotyledons) and amounts to about 78–80% of the original beans treated.

In the next stage, the nib is finely ground between mill stones, or in disc- or roll-type mills; the bulk of the fat, which constitutes from 50 to 55% of the nib, is liberated and melts at the temperature of grinding, so that the resultant material—the "cacao mass" or "liquid nib"—runs from the mill in the form of a thick brown liquid, which sets into a hard block if allowed to cool.

It is common practice nowadays to subject the cacao intended for the manufacture of cocoa to a mild treatment with alkali (solubilising or *opening*, process invented by Van Houten, *v.* COCOA) which may be applied to the roasted bean, the finished cocoa powder, or, as is most usual, to the ground cacao mass; as a rule 2–3% of potassium, sodium, ammonium or magnesium bicarbonate or carbonate are employed. If the process is properly conducted, the treatment does not appreciably affect the free fatty acid content or other characteristics of the fat present in the nib (*cf.* H. Fincke, "Handbuch der Kakaoerzeugnisse," J. Springer, Berlin, 1936).

If the cacao is intended for the production of cocoa powder and cacao butter, the greater part of the fat present is now removed by expressing the hot, liquid mass in hydraulic presses. The usual press consists of a number of superimposed circular pots, which are filled with the mass and separated from each other by perforated plates clad in filter-cloths; temperatures of about 70°–90°C. and pressures up to 6,000 lb. per sq. in. are employed. The expressed fat, which entrains a certain amount of finely divided cocoa particles in suspension, is then filtered and run into suitable receptacles, where it is allowed to cool with occasional stirring. The residual press cakes only require grinding, sifting, and flavouring to convert them into the ordinary domestic cocoa powder. The amount of fat left in the press cake is determined by the quality desired for the cocoa, and is usually about 18–30%, and rarely less than 9%.

Cacao mass is similarly prepared (but with the omission of the alkaline treatment) from cacao beans intended for the manufacture of eating chocolate, but in the case of high-class products, the whole of the fat is allowed to remain in the mass—indeed, it will be necessary to add further quantities of cacao fat when the sugar and other ingredients are incorporated. In England and other countries where the use of cacao butter substitutes is permitted, manufacturers of cheap chocolates may express a portion of the costly cacao fat from the mass and replace it by cheaper substitutes (*see* CHOCOLATE FATS).

The production of cacao butter and cocoa powder are thus complementary; but, whereas in the last century the fat represented merely a by-product of the cocoa industry, the rapid modern increase—particularly since the War—in the consumption of rich chocolate and milk chocolate has resulted in a demand for additional cacao butter which has outstripped the supply from normal cocoa manufacture, with the result that the beans are now often expressed primarily for the sake of the fat. In some cases the beans so intended for the production of fat are not shelled before crushing and pressing; it then becomes possible to employ continuous acting presses of the expeller type (which cannot be used for shell-free cacao mass) for the expression. The fat recovered from unshelled beans may be expected to include a certain proportion of shell-fat and is, of course, excluded from use in chocolate manufacture in those countries which possess food legislation of the type discussed above; the corresponding press-cake or meal can only be employed for industrial purposes or for cattle feeding. (According to Fincke (1936) in certain districts, *e.g.* Spain, beans intended even for chocolate manufacture are not always shelled before grinding.)

The filtered cacao butter obtained by the expression of sound nibs is fit for edible or

pharmaceutical use without further refining. *At ordinary temperatures*, it is a hard, brittle (snappy) fat of a pale yellow colour which fades, however, on exposure to light; it melts readily at 32°–34°C., is easily digested (*cf.* Langworthy and Holmes, U.S. Dept. Agric. Bull. 505, 1917; Gardner and Fox, Biochem. J. 1919, **13**, 368; McClure and Carr, Amer. J. Physiol. 1925, **74**, 70), and possesses a pleasant chocolate-like odour and taste and good keeping properties. The peculiar combination of brittle consistency (snap) and relatively low melting-point, to which cacao butter owes its pre-eminent position as a chocolate and confectionery fat, is due to its consisting predominantly of a mixture of comparatively few individual glycerides (*v. infra*).

The *acid value* of commercial cacao butter of good quality ranges usually from 1·2 to 2·5, and should not exceed about 4·5 for fat from sound beans. Higher acid values are found for fats obtained from damaged, mouldy beans, or recovered from cacao waste, mouldy chocolate, etc. An abnormally low acid value would suggest that the fat had been deacidified artificially, or that the solubilising treatment of the cacao had been misconducted with an excess of alkali; in such a case, the fat should be examined for traces of metallic soaps.

The following analytical figures are collated from analyses of commercial cacao butters by Knapp (*l.c.*) and Fincke (1929, *l.c.*; 1936, *l.c.*; *cf.* Z. Unters. Lebensm. 1928, **56**, 312; *cf.* Lewkowitsch, "Chem. Tech. of Oils, Fats, and Waxes," 6th ed., Vol. II, p. 601, for numerous earlier figures).

TABLE I.

	Knapp.	Fincke.
$d^{99}_{15\cdot5}$	0·858–0·865	—
n^{40}_{D}	1·4563–1·4573	1·4567–1·4578
Saponification value	192–198	192–195·3
Iodine value	34–38	33·5–37·5 (33·5–40 as extremes)
Unsaponifiable matter	0·3–0·8%[1]	—
Melting-point of fat	32°–34°C.	Flow-m.p. 31·7°–33·5°C. Clear-m.p. 32·8°–35·3°C.
Melting-point of the insoluble fatty acids	48°–50°C. (titer-test)	Flow-m.p. 49·4°–51·0°C. Clear-m.p. 51·8°–53·6°C.

[1] 0·3–0·35% in 8 samples examined by Grossfeld (Z. Unters. Lebensm. 1930, **60**, 64), and 0·2–0·41% in the fat from 22 samples of chocolate (*ibid.* 1931, **62**, 441).

The Reichert-Meissl value (0·2–0·5), Polenske value (0·3), Kirschner value (0·5), and Bertram A- and B-values (0·06–0·12, and 0·3–0·6 respectively) are all very low. The thiocyanogen value ranges from 32 to 35 (H. P. Kaufmann, Z. angew. Chem. 1929, **42**, 402).

The considerable *difference figure* between the melting-point of the fatty acids and that of the fat itself (*i.e.* some 17–19 units) is distinctive, and is valued by Fincke as a useful criterion of purity; the presence of foreign vegetable fats may be indicated by a low (or even, in the case of hydrogenated fats, by a negative) figure for this difference. (*N.B.*—It is necessary to keep the sample of cacao fat in the solid state for a considerable time (48 hours) before determining the melting-point.)

The composition of the fatty acids of two samples of cacao butter has been determined by Hilditch as follows: stearic acid, 34·5, 35·4%; palmitic acid, 24·4, 24·4%; oleic acid, 39·1, 38·1%; linolic acid, 2·0, 2·1% (Hilditch and Lea, J.C.S. 1927, 3106; Hilditch and Stainsby, J.S.C.I. 1936, **55**, 95T; *cf.* Lea, J.S.C.I. 1929, **48**, 41T); comparable figures have also been obtained by less exact methods by Amberger and Bauch (Z. Unters. Nahr. Genussm. 1924, **48**, 37) and Grossfeld (Kazett, 1930, **19**, 178 *et seq.*; *cf.* Z. Unters. Lebensm. 1930, **60**, 72). From the iodine and thiocyanogen values Kaufmann (Z. angew. Chem. 1929, **42**, 402) calculates the proportion of oleic and linolic acids in the fatty acids of nineteen samples of cacao fat as 34–38% and 2–5% respectively. The statements in the older literature (*cf.* Graf, Arch. Pharm. 1888, **226**, 830) that arachidic acid occurs in cacao fat appear to be erroneous (Morgan and Bowen, J.S.C.I. 1924, **43**, 346T; Lüning and Drude, Z. Unters. Lebensm. 1931, **61**, 491).

An elaborate examination of the constituent glycerides of cacao butter by Hilditch and Stainsby (*l.c.*) suggests that the fat consists almost entirely of the mixed glycerides of the saturated and unsaturated fatty acids, as follows:

TABLE II.

Glyceride.	% of fat.	Configuration of glyceride.
Oleo-palmito-stearin	52	Probably both the α-palmito- and β-palmito-isomerides.
Oleo-di-stearin	19	Probably mainly β-oleo-distearin.
Stearo-di-olein	12	Both α- and β-stearo-di-olein.
Palmito-di-olein	9	—
Oleo-di-palmitin	6	Probably mainly β-oleo-di-palmitin.
Palmito-stearins	2	Mainly di-palmito-stearin.

NOTE.—In the above analysis the small proportion of linolic components in the fat is not considered separately, but is included in the oleo-glycerides.

A hydrocarbon (probably identical with amyrilene, $C_{30}H_{48}$) and two sterols, m.p. 146°C. (162°–163°C. after regeneration from the di-bromo-acetate), and m.p. 136°–139°C., respectively, were isolated from the unsaponifiable matter of cacao butter by Matthes and Rohdich (Ber. 1908, **41**, 19, 1591; *cf.* Procknow, Dissert. Würzburg, 1909), *whilst* H. Labbé, H. de Balsac, and Lerat (Compt. rend. 1929, **189**, 864; Bull. Soc. Thér. 1930, [ii], **35**, No. 4, 71; *cf.* F.P. 700036) have identified two sterols, *α-theosterol*, m.p. 115°C., and *β-theosterol*, m.p. 134°C.; β-theosterol is stated to acquire anti-

rachitic activity after irradiation with ultra-violet light. Cacao butter is also stated to possess weak vitamin-A activity (Labbé, H. de Balsac and Lerat, Bull. Soc. Thér. 1930, [ii], No. 10).

Traces of *theobromine* are found in cacao butter, whether it be obtained by expression or by extraction with certain solvents.

Expressed cacao butter contains only traces of phosphatides (less than 0 12%; *cf.* Winkler and Sale, J. Assoc. Off. Agric. Chem. 1931, **14**, 537; Avent and Morgan, J.S.C.I. 1932, **51**, 169T; Rewald and Christlieb, Z. Unters. Lebensm 1931, **61**, 520; Chem. Ztg. 1931, **55**, 393; Fincke, *l.c.* 1929, p. 119), although about 0 4% can be extracted from the roasted bean by solvents (*cf* Nottbohm and Mayer, Z. Unters. Lebensm. 1933, **65**, 55); a somewhat higher content of phosphatides may be expected in the fat extracted from fabricated chocolate, since it is current practice to add from 0 5 to 1 0% (calculated on the fat) of vegetable lecithin to the chocolate during manufacture. The addition of lecithin to the "mass," in order to facilitate the expression of the fat, has been patented (Hanseatische Muhlenwerke A.-G., B.P. 360332). (For the detection of soya bean oil in fat containing soya lecithin, *see* Auerbach, Fettchem. Umschau, 1933, **40**, 218) Lower grades of cacao fat may be obtained by pressing or by solvent extraction from damaged cacao beans or from chocolate manufacturers' waste—nib-fragments, shells, and germs (*v. infra*). It is stated that a certain amount of cacao fat is recovered in Holland by solvent extraction from sound cacao, from which a first charge of fat has been obtained by expression.

Edible cacao fat is chiefly employed in the manufacture of chocolate, but a certain amount is used in other confectionery. During 1917–1918 cacao butter made a brief appearance on the market as a domestic cooking fat, although attempts made at that time to remove the characteristic aroma were not very successful (*cf.* Martin and C.W.S., Ltd., B.P. 122512/1918). However, by refining and deodorising extracted cacao butter of fair quality, a flavourless product may be obtained which appears to be used to some extent for edible purposes in cheap chocolates, confectionery, etc., and perhaps in pharmacy. As stated above, however, the use of extracted cacao fat for chocolate manufacture is forbidden in certain countries. A colourless, deodorised product is now being offered for the pharmaceutical uses—cosmetics, suppositories, etc.—to which cacao butter has long been applied. Cacao butter is also employed in the *enfleurage* process for the extraction of essential oils.

Cacao Shell Fat, Cacao Germ Fat.—The shells of the raw cacao bean contain some 1–2% of fatty matter and the germs about 3% (Fincke, *l c.* 1936, p. 303), but during the process of roasting, a certain amount of the nib-fat diffuses into the other tissues, with the result that some 3–8% of fat can be extracted from the shells of the roasted beans, and about 3 5% from the germs. A still higher proportion of fat (*e g.* 5–15%) may be obtained from the shells and germs as separated commercially in the factory, since these fractions normally include a considerable proportion of fine nib-fragments. Owing to the presence of extracted impurities, the shell and germ fats are yellow-brown in colour and possess a disagreeable odour and taste; they are softer than cacao butter and possess a higher iodine value and a greater content of unsaponifiable matter (*cf.* Table III). The acid value is high, unless the fat has been artificially de-acidified. Cacao shell fat has, however, been refined and sold for edible purposes.

TABLE III.

	Cacao shell fat [1]	Refined cacao shell fat.[2]	Cacao germ fat.[3]
n_D^{40} . .	1 4570–1 4630	1 4585, 1 4641	1 4620–1 4676
Melting-point	28 0°–35°C.	—	about 30 5° (but sets with difficulty)
Flow m p	31°–32°C.	32 2°, 31 5°	—
Clear m p	38°–40°C.	43°–45°, 48°–50°	—
Acid value	7–70	1 7, 2 3	21–40
Saponification value	177 0–189 8	189 9, 202 1	178–181 (170 Härtel)
Iodine value .	39–55 5 (usually 40–50)	39 9, 41 2	50 8–70 0
Unsaponifiable matter %.	2 5–2 6 (2 samples only)[4]	1 6, 5	—

[1] Lewkowitsch, "Oils, Fats, and Waxes," 6th ed., Vol. II, p 595; Härtel, Z Unters Nahr. Genussm. 1924, **47**, 264; Galanos, *ibid* 1924, **48**, 212; Fincke, *ibid* 1925, **50**, 205; l'Heureux, Bull. agric. Congo belge 1931, **22**, 498.

[2] Two samples: H. Fincke, "Kakaobutter u. ihre Verfälschungen," Stuttgart, 1929, p. 148.

[3] Twelve samples of germs hand separated from (raw and roasted ?) beans: H. Fincke, "Handbuch der Kakaoerzeugnisse," Berlin, 1936, p. 303; *cf.* Fincke, *l c* 1925, Härtel, *l c* 1924

[4] The figure of 7 5–9% on the fat from unroasted shells given by Labbé, H. de Balsac, and Lerat (Comp rend 1929, **189**, 864) requires confirmation. 8 8% of unsaponifiable matter has been found in a sample of fat extracted by light petroleum from pure cacao shell by Vizern and Guillot (Ann. Falsif. 1936, **29**, 484).

The fatty acids from a sample of cacao shell-fat examined by Schmitz and Kaufmann (*cf.* Fincke, *l.c.* 1936, pp. 303–4) were found to consist of 54% of saturated (stearic and palmitic) acids, 40 4% of oleic acid, and 5 6% of linolic acid; the presence of solid unsaturated fatty acids is reported by Kupferberg (Thesis, Berlin, 1932; through Fincke, *l.c.*).

Fincke (*l c.* 1929, p. 153) stated that extracted cacao shell fat may contain up to 1% of a crystalline substance (m.p. 115 5°–116 5°C.) insoluble in light petroleum, of which only traces (0 013%) could be found in expressed cacao butter; it seems possible that this substance is identical with α-theosterol (m.p. 115°C.), since Labbé notes that the theosterols occur in much greater concentration in the shell fat than in the nib-fat. Cacao shell fat exhibits a considerable vitamin-D potency (*cf.* S. K. Kon and K. M. Henry, Biochem. J. 1935, **29**, 2051; A. W. Knapp and Coward, *ibid.* 2728; Analyst, 1934, **59**, 474).

Cacao butter, being very high in price, is liable to adulteration or substitution by chocolate fats of similar physical characters. Tallow and paraffin wax, which were formerly employed as adulterants, are easily detected and hence have disappeared. Small additions of bleached beeswax are still occasionally employed as a stiffener in chocolate and are easily detected by the increase in unsaponifiable matter and the clear melting-point. Fats of the coconut oil group are revealed by high figures for the Polenske and Bertram A-values, and an estimate of the amount of such addition may be obtained by calculations based on these figures, as in the determination of coconut oil in margarine (*cf.* Baumann, Kuhlmann, and Grossfeld, Z. Unters. Lebensm. 1926, **51**, 27 ; Kuhlmann and Grossfeld, Z. angew. Chem. 1926, **39**, 24 ; Klostermann and Quast, Z. Unters. Lebensm. 1927, **46**, 297). It must be remembered, however, that frequently hydrogenated or pressed coconut oil (*coconut stearin*), etc., is employed, the characteristics of which differ somewhat from the typical figures for the original fat which form the basis of the standard calculations.

A qualitative test for the presence of palm-kernel or coconut oils, etc., originally proposed by Cohn (Z. angew. Chem. 1924, **37**, 304 ; *cf.* Baughman, J. Assoc. Off. Agric. Chem. 1925, **8**, 703 ; Sale, *ibid.* 1931, **14**, 526) has been adopted as a tentative method by the American Association of Official Agricultural Chemists (" A.O.A.C. Standard Methods," 1935, p. 201): 5 g. of the fat are saponified with 15 c.c. of alcoholic potash (25 g. per 200 c.c.); the soap is evaporated to dryness on the steam-bath, re-evaporated after the addition of 5 c.c. of water in order to remove all the alcohol, and then dissolved in 100 c.c. of water; 100 c.c. of a saturated solution of sodium chloride are mixed in, and after standing for 15 minutes the solution is filtered through a Buchner filter ; 100 c.c. of the filtrate are treated with a further 100 c.c. of the salt solution as above and filtered ; this second filtrate is neutralised to phenolphthalein with dilute hydrochloric acid (1+3) and 0·5 c.c. of the acid is added in excess ; the solution remains clear if the sample consists of pure cacao butter but becomes turbid if coconut oil, etc., is present. A blank test with authentic cacao butter should be carried out for comparison. Any milk fat present (as would be the case, for example, in the fat extracted from a milk chocolate) also produces an opalescence or turbidity ; in this case the approximate percentage of milk fat may be calculated from the lactose or casein content of the chocolate, and a matching mixture of butter fat and cacao fat used for the blank test.

The amount of butter fat in the fat may also be determined by methods based on determinations of the Reichert-Meissl and Kirschner values, or of the butyric acid value, or Bertram B-value of the sample (*cf.* references under discussion of detection of coconut oil (*supra*), Kulhmann and Grossfeld, Z. Unters. Lebensm. 1926, **51**, 31 ; Grossfeld and Wissemann, *ibid.* 1927, **54**, 352; Grossfeld, *ibid.* 1935, **70**, 459).

Admixture of hydrogenated oils to cacao butter lowers the difference value between the melting-points of the fat and its fatty acids, and may also be revealed by the detection of *iso*-oleic acid or (occasionally) of traces of nickel (*cf.* H. P. Kaufmann, Chem. Umschau, 1930, **37**, 49, 72).

The detection of illipé (Borneo) tallow (*q.v.*) and similar " green butters " (*i.e.* vegetable tallows which may be coloured artificially to resemble Borneo tallow), which are largely used as substitutes for cacao butter, is a more troublesome matter, and no single method is available which is entirely satisfactory in the case of mixtures. The original Halphen test (J. Pharm. Chim. 1908, **28**, 346) for these products may fail with the modern refined Borneo tallow (Knapp, Moss, and Melley, Analyst, 1927, **52**, 452). The addition of these fats to cacao butter modifies the ordinary characteristics to some extent, the effect on the melting-point data being as a rule the most significant (*cf.* Knapp, Moss, and Melley, *l.c* ; Vizern and Guillot, Ann. Falsif. 1936, **29**, 484 ; Tate and Pooley, Analyst, 1921, **46**, 229 ; Bywaters, Maggs, and Pool, *ibid.* 1927, **52**, 324). Fincke (*l.c.* 1929, 1936) particularly values the indications afforded by a determination of the differences between the melting-points of the fat and its fatty acids, or between the numerical figures for the melting-point and iodine value of the fatty acids ; others prefer to draw conclusions from the characteristic shape of the cooling (freezing-point) curve of the fat (*cf.* Pichard, Ann. Falsif. 1923, **16**, 197 ; Bull. Off. Off. Int. Fab. Cacao et Choc. 1931, **1**, 95, 157, 245 ; 1932, **2**, 29 ; van Roon, Chem. Weekblad. 1929, **26**, 619 ; 1930, **27**, 498 (dilatometric method) ; Avent, Analyst, 1930, **55**, 477 ; Vivario, Congrès Int. Fabr. Chocolat et Cacao, Antwerp, 1930, vol. préparatoire, p. 171).

The resistance to bleaching by light of the natural colouring matter of Borneo tallow may also serve as an indication of its presence (Knapp, Moss, and Melley, *l.c.*). Turbidity tests based on the critical temperatures of solution of the various fats in ether, aniline, etc. (*cf.* Marange, Ann. Falsif. 1923, **16**, 454 ; Assoc. Off. Agric. Chem. " Official Methods," 1935, p. 201 ; *cf.* J. Assoc. Off. Agric. Chem. 1930, **13**, 486), appear to be less useful.

Tables compiled by Fincke (" Kakaobutter u. ihre Verfälschungen," 1929, pp. 191 *et seq.*) illustrating the characteristics of mixtures of cacao fat with almond, walnut, and hazel-nut oils, and/or milk fat afford useful data in connection with the examination of the fat from nut or nut milk chocolate ; the presence of coffee in chocolate may cause a slight increase in the iodine value of the fat (Fincke, *l.c.* p. 214).

The detection of small quantities of extracted cacao fat (which is usually derived from the waste shells or germs) is probably the most difficult problem of all, since apart from their high acid value (which can be reduced by de-acidification and refining) these fats do not differ very greatly from the nib fat in chemical properties. The following test for extracted cacao shell fat (due to Fincke) has been accepted provisionally as an official test in Germany : 5 c.c. of the melted cacao butter are treated with 1 c.c. of a 2:1 mixture of fuming hydrochloric acid and nitric acid (d=1·45) at 50°–70°C. ; a

red brown coloration indicates the presence of the shell-fat (*cf. also* Aufrecht, Chem. Ztg. 1929, 53, 318; Schmandt, Z. angew. Chem. 1929, 42, 1039).

Of the world exports of about 560,000 tons per annum of raw cacao, about 47% (on the whole raw bean) represents the contained fat. On the same basis, the home consumption of raw cacao of the United Kingdom in 1936, which mounted to some 102,000 tons, corresponded to about 47,940 tons of cacao butter: to this must be added imports of cacao butter which ranged from 6,407 tons (value £396,052) in 1934 to 8,660 tons (value £572,890) in 1936, of which about 84% and 96% respectively were derived from the Netherlands. Domestic exports (including re-exports, which were negligible) amounted to about 500 tons in 1934, 1,000 tons in 1935, and 2,000 tons in 1936 (valued at £36,500, £75,000, and £152,000 respectively). Holland is the largest exporter of manufactured cacao butter, 17,830,447, 20,954,417, and 22,641,747 kg (valued at 2,461,257, 3,176,628, and 3,986,126 guilders) being exported to all parts of the world in 1934, 1935, and 1936 respectively. E. L.

CACAO RED. A blood red powder obtained by Reutter (Compt rend. 1913, 156, 1842; Chem. Zentr. 1913, ii, 518) on hydrolysing a crystalline product *cacaorin*, $C_{16}H_{20}O_6N_8$, m.p. 184°–185°; the red powder yields glucose, CO_2 and cacao brown when treated with H_2SO_4.

Fincke (Z. Unters Lebensm. 1928, 55, 559; Chem. Zentr. 1928, ii, 2300) describes cacao red as very soluble in alcohol, red if acid, violet when neutral and green if alkaline. Cacao brown dissolves in aqueous alkali with a brown colour.

Heiduschka and Bienert (J pr. Chem. 1927, [ii], 117, 262; 1928, [ii], 119, 199) put forward in their second paper the formula $[C_{21}H_{21}O_{13}]_x$, and the constitution of a derivative of 3′ 4′:3.5.7-pentahydroxy-6 8 dimethyl-2 3-dihydroflavone. Heiduschka and Bienert in their first paper obtained cacao red 1·8–2% from cacao beans (not defatted) as an amorphous powder of a fine red colour, which carbonises when heated without melting. Very hygroscopic, astringent taste Gives no sugar when heated with water or with dilute sulphuric acid. Its solutions are colloidal and without dyeing properties (*cf.* Wehmer, Pflanzenstoffe, 1931, ii, 773).

CACHALOT OIL. Oil obtained from the blubber of the cachalot. (For its properties and composition, *v.* Fendler, Chem.-Ztg. 1905, 29, 555.)

CACHOU DE LAVAL. The earliest sulphide dyestuff, a direct cotton dye prepared by heating sawdust, bran, etc., with sulphur and sodium sulphide.

CACODYL CARBIDE

$$(CH_3)_2AsC\,CAs(CH_3)_2$$

v. ARSENICALS, ORGANIC.

CACODYLIACOL. Guaiacol cacodylate, $(CH_3)_2AsO\cdot O\cdot C_6H_4(OCH_3),H_2O$.

CACODYLIAGOL. *Cacodyliacol.* Syn. for guaiacol cacodylate.

CACODYLIC ACID, dimethylarsinic acid, $Me_2AsO\cdot OH$ (*v.* ARSENICALS, ORGANIC). The sodium salt is used in medicine.

CACOTHELINE, $C_{20}H_{22}O_5N_2(NO_2)_2$, is a nitro derivative of brucine employed as a spot test for tin (*v.* CHEMICAL ANALYSIS and Ind. Eng. Chem. [Anal.] 1935, 7, 26).

CADALENE. 1:6-dimethyl-4 *iso*propyl-naphthalene is a liquid, b.p. 157°–158°/12 mm. obtained by dehydrogenation of cadinene with sulphur (Ruzicka and Meyer, Helv. Chim. Acta, 1921, 4, 505), and is the first naphthalene hydrocarbon to be prepared from a sesquiterpene.

CADAVERINE. Pentamethylenediamine, $NH_2\cdot[CH_2]_5\cdot NH_2$.

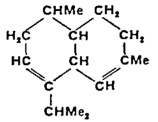
CADE, OIL OF (Juniper Tar Oil). An almost black oil, obtained by the destructive distillation of the wood of *Juniperus oxycedrus*, a tree growing in the countries of the West Mediterranean. The oil, sp.gr. 0 975–1·010, contains a sesquiterpene, *cadinene*, $C_{15}H_{24}$, and is used in chronic skin diseases (B.P.C. 1934).

CADECHOL. A molecular compound of camphor and deoxycholic acid.

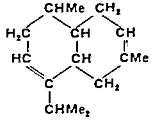
CADET'S FUMING LIQUID or ALKARSIN. A brown spontaneously inflammable oil obtained (1760) by distilling potassium acetate with arsenious oxide. Bunsen showed that it contained cacodyl oxide, $(Me_2As)_2O$ (*v.* ARSENICALS, ORGANIC).

CADIE GUM. Synonym for gamboge

CADINENE.

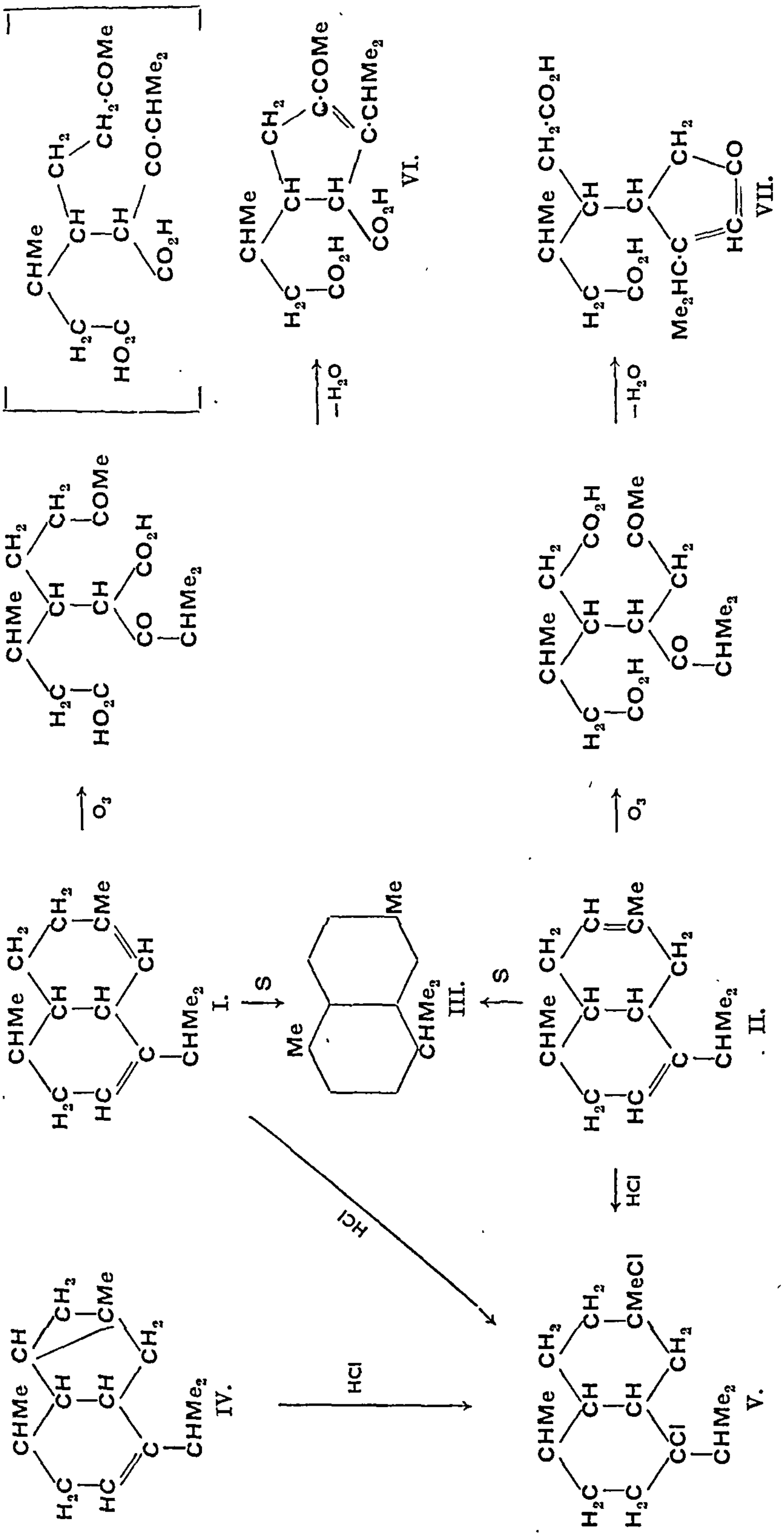


α



β

The sesquiterpene hydrocarbon, *cadinene*, $C_{15}H_{24}$, b.p. 134°–136°/11 mm., d_4^{20} 0·9319, n_D^{20} 1·5079, $[\alpha]_{5461}$ −125 2° (Henderson and Robertson, J.C.S. 1924, 125, 1992), occurs very widely distributed in nature. It forms the main sesquiterpene constituent of oil of cubebs, galbanum oil, and oil of cade. The dextrorotatory form, b.p. 139°–140°/13 mm., $d^{16°}$ 0·9260, $n_D^{16°}$ 1·50934, α_D +38 72°, has been isolated by Deussen (J. pr. Chem. 1928, [ii] 129, 121) from West Indian sandalwood oil. The



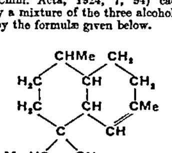
hydrocarbon is best identified by the preparation of the *dihydrochloride*, m.p. 117°–118°, $[\alpha]_D$ −36 24°; the *dihydrobromide* has m.p. 124°–125°, the *dihydroiodide*, m.p. 105°–106°, the *nitrosochloride*, m.p. 93°–94°, and the *nitrosate*, m.p. 105°–110°. If cadinene is treated with the Bertram-Walbaum reagent or heated with formic acid at 100° it is isomerised to iso*cadinene*, b.p. 124°–126°/11 mm., d^{20} 0·914, n_D^{20} 1·515 (Henderson and Robertson, J.C.S. 1924, 125, 1992; 1926, 2811; Robertson, Kerr and Henderson, *ibid.* 1925, 126, 1946) which is probably identical with the hydrocarbon separated by Tröger and Felman (Arch. Pharm. 1898, 236, 692) from oil of cade. This hydrocarbon has been prepared also by Ruzicka and Capato (Helv. Chim. Acta, 1925, 8, 289) from nerolidol and bisabolene.

Cadinene has been shown to be a mixture of the two hydrocarbons represented by (I) and (II). On dehydrogenation with sulphur it yields cadalene (1:6 dimethyl-4-*iso*propylnaphthalene) (III), whilst on catalytic hydrogenation it gives *tetrahydrocadalene*, $C_{15}H_{28}$, b.p. 125°–128°/10 mm., d^{20} 0·8038, n_D^{20} 1·48045, α_D −20°, thus proving the presence of two ethylenic linkages, which cannot be conjugated since cadinene is not reduced by sodium and alcohol. One of the ethylenic linkages must be adjacent to the *iso*propyl group, since copaene (IV) gives with hydrogen chloride cadinene dihydrochloride (V). An investigation by Ruzicka and Stoll (Helv. Chim. Acta, 1924, 7, 86) has shown that cadinene on ozonolysis gives a mixture of two dibasic keto-acids, $C_{15}H_{22}O_5$, which are probably represented by (VI) and (VII) being derived from the hydrocarbons (I) and (II) as indicated in the scheme given on p. 189.

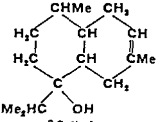
J. L. S.

CADINOL. The dextrorotatory form of the sesquiterpene alcohol, *cadinol*, $C_{15}H_{26}O$, b.p. 155°–156°/12 mm., d_{14}^{14} 0 9665, n_D^{14} 1·5054, α_D +7·7°, was isolated by Semmler and Jonas (Ber. 1914, 47, 2073) from galbanum oil (from *Peucedanum galbaniflum* and *P. rudicaule*), whilst Henderson and Robertson (J.C.S. 1926, 2811) showed the lævorotatory alcohol ($[\alpha]_D$−5 4°) to be present in oil of cubebs. The presence of these alcohols has been observed also in other oils.

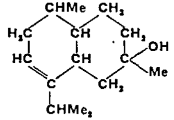
Cadinol is a tertiary alcohol yielding cadalene on de-hydrogenation. On treatment with hydrogen chloride cadinene dihydrochloride is obtained. According to Ruzicka and Stoll (Helv. Chim. Acta, 1924, 7, 94) cadinol is probably a mixture of the three alcohols represented by the formulæ given below.



α-Cadinol.



β-Cadinol.



γ-Cadinol.

J. L. S.

CADMIUM (*Kadmium*, Ger.) Sym. Cd. At. wt. 112·41, at. no. 48. Isotopes, 106, 108, 110, 111, 112, 113, 114, 116.

History.—The metal cadmium is of comparatively recent discovery, for it was unknown before 1817, in which year Stromeyer obtained it from its oxide, having been led to this discovery by observing the yellow colour of a sample of zinc carbonate which was not due to iron. At about the same time Hermann found that certain samples of zinc oxide when dissolved in hydrochloric acid gave a yellow precipitate with hydrogen sulphide, and that this precipitate was the sulphide of a new metal with properties similar to those observed by Stromeyer.

Occurrence.—Cadmium occurs in very small quantities as sulphide, CdS, in *greenockite*, which is a yellow mineral, giving a streak between orange-yellow and brick red. It often occurs as a coating on zinc ores, and the chief localities for its occurrence are Bishopton (Scotland) Přibram (Czechoslovakia), and Friedensville (Pennsylvania). Cadmium occurs in small quantities, probably as sulphide also, in zinc sulphide ores, and the metal is obtained as a by-product during the extraction of zinc by distillation or wet methods from these ores in which it is present up to an amount of about 0 4%. It occurs also in carbonates and silicates of zinc, and is found in most samples of commercial zinc obtained by distillation methods.

Cadmium is also recovered during the treatment of certain ores of lead and copper. In the case of lead ores containing zinc, these may contain cadmium up to 0 02%. Small as this percentage is, the metal becomes concentrated in the fumes from the blast-furnace smelting of the ore for lead, and cadmium is found in appreciable quantities in the dust obtained from the bag-house filtration plant. A small quantity of cadmium also finds its way into the lead or base bullion obtained by the smelting of such ores and this is concentrated in the vat residues resulting from the electrolytic refining of the lead. In the case of copper ores associated with zinc minerals, a small amount of cadmium is

frequently present, and here again during the blast-furnace smelting of these ores the cadmium becomes concentrated in the dust obtained by the bag-house filtration of the furnace waste gases. Cadmium has also been found in coal and in the ash of coal, for example, Richardson reported 1·21% CdO in the ash of coal from Berwick, Scotland (Jahresbericht, 1847–8, **1**, 1120). Certain strongly acid mine waters in the Joplin district contain sulphuric acid, zinc sulphate, and small quantities of cadmium sulphate, the last of which has also been reported as present in mine waters in the Missouri zinc region. Hillebrand reported 0·1% Cd in the waters of a spring on Shoal Creek, Missouri (Bull. U.S. Geol. Survey, 1893, **113**, 49).

In recent years the demand for cadmium and its compounds has increased enormously, and the chief producers have been U.S.A., Canada, France, Belgium, Australia, Norway and Poland. There are potential supplies of the metal in Italy, also from zinc ores, and another source is the accumulated flue dust at the Otavi mines at Tsumeb (British South-West Africa), shipments of which have already been made to Germany for treatment. Cadmium is also recovered in this country during the purification of zinc sulphate, in the manufacture of lithopone, and from various residues of zinc extraction processes.

Preparation.—(*a*) Cadmium was formerly obtained from the first portion of distillate during zinc ore reduction. In the reduction in retorts of the zinc oxide produced from zinc ores the first portions of the distillate consist of a mixture of the metals zinc and cadmium and their oxides, but contain a higher percentage of cadmium (on account of its higher volatility) than the original ore. By collecting this material, mixing with fine coke, and submitting it to further distillations, at a dull red heat (800°), cadmium containing a little zinc is obtained which may be further purified by distilling *in vacuo*. E. A. Partridge obtained spectroscopically pure cadmium by redistillation *in vacuo* nine times (Amer. J. Sci. 1890, **40**, 377). (*b*) From the wet process of zinc extraction. The greater part of the cadmium recovered is now obtained as a by-product during the treatment of zinc ores for the electrolytic deposition of the zinc. The zinc concentrates are roasted and leached with sulphuric acid. After removal of copper from the solution thus obtained, any cadmium present is precipitated by means of zinc dust. The metal is thus obtained as a spongy mass which is partially oxidised, dissolved in sulphuric acid, and the cadmium deposited electrolytically, an anode of ferrosilicon and a cathode of cadmium being used, this cathode having been previously deposited on metallic aluminium and removed therefrom. The deposited cadmium is melted down in an electric furnace under caustic soda and cast into sticks.

Flue-dusts, bag-house products, etc., containing cadmium are treated in a similar manner.

At the works of the National Smelting Co., Avonmouth, various residues from the zinc smelting process are treated as above for the recovery of cadmium sponge, which is then submitted to distillation yielding metal containing over 99·95% Cd (Metal Ind. 1937, **50**, 113).

Detection and Estimation.—*See* CHEMICAL ANALYSIS (pp. 567, 580, 590, 654, 700).

Spectrography.—A. de Gramont, using a quartz spectrograph, found the most sensitive rays to be 2,288·0 and 2,265·0, the latter being the last to disappear (Twyman, " Wave Length Tables," A. Hilger, London, 1931). By using the line 2,288·0, it was found possible to determine from 0·001 to 0·75% cadmium in zinc, using tin lines as supplementary standards of intensity. It is also estimated that about 0·00005% cadmium can be detected with certainty in lead samples, using the arc method (" Metallurgical Analysis by the Spectrograph," D. M. Smith, Brit. Non-Ferrous Metals Research Assoc., 1933).

Properties.—Cadmium has a white colour with a tinge of blue, a metallic lustre, and takes a high polish. It is soft, giving a metallic streak on paper but less readily than lead ; it is harder than tin and softer than zinc. It is ductile and malleable and may be drawn into fine wire or hammered into thin leaves. When heated to 80° it becomes brittle and may be powdered in a mortar. When pure it crystallises in hexagonal pyramids and emits a crackling noise like tin when bent and gives a brilliant crystalline fracture. It has been contended that there are two allotropic modifications of cadmium with a transformation temperature of 37·5° or 60°, although opinions are divided on this point. Recent work by Owen and Roberts on the thermal expansion of the crystal lattices of cadmium gives no evidence of such a change (Phil. Mag. 1936, [vii], **22**, 146, 290).

Cadmium melts at 320·9° and boils under atmospheric pressure at 767°. Its vapour is yellowish-brown and at 1,040° the vapour density is 3·94 referred to air and 56·3 referred to hydrogen, suggesting that at that temperature cadmium is monatomic. The latent heat of fusion is 13·0 g.-cal. and of vaporisation (calculated from vapour pressure) is 251 g.-cal. The specific heat of the solid metal varies from 0·0019 at 10°K., 0·0474 at 100°K., 0·0527 at 200°K., 0·0552 at 300°K., 0·0617 at 594°K. (solid) to 0·0667 at 594°K. (liquid) (F. Lange and F. Simon, Z. physikal Chem. 1928, **134**, 374). Other results give from 0·0551 at 75°C. to 0·0620 at 300°C., that of the liquid metal between the temperatures of 350° and 600° is 0·0617 g.-cal. per degree C. (S. Umino, Sci. Rep. Tôhoku, 1926, **15**, 597).

The cast metal has a density of 8·648, which may be increased by cold work (rolling, hammering, etc.) to 8·6944. By heating cadmium in a cadmium sulphate solution at 60°–70° for 12 hours the density fell from 8·655 to 8·648 (A. C. Egerton and W. B. Lee, Proc. Roy. Soc. 1923, (A), **103**, 48). The shrinkage on solidification is 4·74%. The Brinell hardness of cast cadmium is about 21–23 kg. per sq. mm. under a load of 500 kg. applied by a 10 mm. ball for a period of 2 minutes. The effect of forging or rolling the metal is to increase its hardness at first, the maximum hardness value being reached about 1 day after the operation, then rapid softening proceeds for a period of from 10–100 days, the

worked metal becoming ultimately softer than the cast material. The tensile strength of the cast metal varies from 3·75 to 4·7 tons per sq in. with an *elongation of 66–46%*. *The effect of* cold work is to increase both tensile strength and elongation, but long ageing after work hardening causes a reduction to figures below those obtained for the cast metal (C. H. M. Jenkins, J. Inst. Metals, 1931, **45**, 307).

The thermal conductivity of the metal is 22 g.-cal. per cu.m. per degree per sec, and the electrical resistivity in microhms per cm.^{3} at 20°C. for extruded rod is 6 85 and for drawn wire 7·59; at 100° for extruded rod 9 03, and for drawn wire 9 94 (Jenkins). The linear expansion coefficient at 0°–100° is 0 0000306. The surface tension of liquid cadmium varies from 570 dynes per cm at 330° to 597 at 400°. Cadmium is diamagnetic. Colloidal cadmium may be obtained by sparking under water using a cadmium cathode.

When heated in air to a temperature of 300° a brown oxide layer is formed on the surface of the metal accompanied by a weight increase during the first 50 hours of heating, after which time further heating, even up to 400 hours, gives no increase in oxidation, the layer of oxide becoming impervious (Pilling and Bedworth, J. Inst. Metals, 1923, **29**, 575). On heating to higher temperatures cadmium burns, evolving brown fumes of oxide. Moist air oxidises the metal superficially, covering it with a greyish-white film. The metal does not decompose water at 100°, but cadmium vapour decomposes steam forming the oxide and liberating hydrogen. When finely divided cadmium is moistened with a 10% solution of sodium or potassium hydroxide in the presence of air or oxygen and the excess moisture removed by pressing, a reaction occurs with incandescence and the metal is completely converted into oxide (W. S. Sebborn, Trans. Faraday Soc. 1933, **29**, 659). The metal is attacked readily by hydrochloric, sulphuric and especially by nitric acid, and dissolves slowly in acetic acid. It combines directly with the halogens (in aqueous solution) and forms double salts with potassium, calcium, magnesium, etc. Its salts, especially the iodide, are but slightly dissociated in solution, and hence precipitation of the metal is usually incomplete. The salts, the vapour of the metal, and that of the oxide are poisonous and cause severe diarrhœa, violent vomiting, and dryness of the mouth and throat.

Alloys.—Small amounts of cadmium with *copper* increase the mechanical strength, *e.g.* 0 98% Cd increases that of hard drawn copper wire 80% while decreasing the electrical conductivity only 14·5%. Thus copper containing 0 8–1 0% Cd is reported to have the best combination of electrical and mechanical properties of any material available for trolley wires and other electrical purposes (G. W. Preston, Elec. Rev. 1935, **116**, 372). Even 0·15% Cd in copper stabilises the work-toughening of the metal under exposure to heat (up to 300°), such as may be caused, for example, by a short circuit. The compounds Cu_2Cd and Cu_2Cd_3 were indicated in the earlier work on the cadmium-copper series (Sahmen, Z. anorg. Chem. 1906, **49**, 301), but later work by Jenkins and Hanson shows that there are six primary constituents capable of separating from the liquid state and that there are two *eutectics, one containing* 39% Cu *at 544°* and the other 1·2% Cu at 314° (J. Inst. Metals, 1924, **31**, 257); the alloys rich in cadmium are steel grey and soft, but harden as copper is increased up to 26 5%, after which the hardness decreases and the copper colour appears. Cadmium alloys containing more than 80% *silver* give uniform and homogeneous metal better suited for trial plates for silver coinage and silverware than the corresponding copper-silver alloys. The low silver alloys take a high polish, tarnish less than silver, and are used for mirrors; these alloys may be deposited electrolytically. Silver alloys containing up to 25% cadmium are used for silver plating, and silver-cadmium alloys containing some copper are white and used by jewellers for plate and wire. An alloy containing Cd 97·5, Ag 2·25, Cu 0·25% has been used for bearings in automobiles. Cadmium forms amalgams with *mercury*, formerly used by dentists but now largely abandoned as they cause a discoloration of the dentine. The *cadmium-nickel* series shows a eutectic at 0·25% Ni at 318°, consisting probably of Cd and $NiCd_7$ (C. E. Swartz and A. J. Phillips, Amer. Inst. Min. Met. Eng 1934, **111**, 333). Cadmium-nickel alloys containing 1–2% nickel are used for bearing metals and have good frictional properties. Owing to their relative high melting point and wear resistance they are suitable for bearings of high-compression type engines, motor cars, etc. A 1·35% Ni alloy casts easily, bonds readily to the common backing material, is not easily oxidised, and its hard constituent $NiCd_7$ does not scratch the softest steel: this is being manufactured under licence in this country under the name "Asarcoloy."

With *zinc* there is a eutectic 83 5% Cd, m.p. 263°, and the high cadmium alloys are used as substitutes for brazing metal for cases in which the ordinary working temperature would affect the properties of the brazed metal. These alloys are considerably stronger than the lead tin solders. The addition of cadmium to brass above 1 0–1·5% materially reduces the strength, *e g.* 4% cadmium practically destroys the strength of a 70% Cu, 30% Zn brass. Cadmium is sometimes used as a partial or total substitute for tin in lead-tin solders and cadmium-lead alloys containing 82–97·5% lead have been recommended for bearing metals. The ternary bearing metal Cd 96·7, Cu 3·1, Mg 0 2 is of high class, having a greater hardness, higher melting-point and lower coefficient of friction than the tin-base bearing metals. It does not begin to distort under a pressure $<$2,500 lb. per sq. in. as against a pressure $<$1,500 lb. per sq. in. for the tin-base alloys and is used for automobile crankshaft and other bearings. One of the specifications of the British Non-Ferrous Metals Research Association for cable sheathing to resist the cracking tendency consists of lead containing 0 25% Cd and 0·5% Sb. Cadmium enters into the composition of a large number of ternary and quaternary alloys containing bismuth, many of which melt below 100° (*v.* Bismuth, Alloys of Bismuth).

Cadmium is used in a number of alkaline cells and accumulators; a primary cell giving a large ampere-hour output at a low but constant E.M.F. was described by Edison in 1900; cadmium amalgams are used in standard cells employed in standardisation and testing as they are capable of giving a constant E.M.F. independent of varying conditions. Alkaline accumulators for which cadmium is required are largely used and have distinct advantages over ordinary lead cells, as they may be completely discharged or allowed to remain charged without attention and with no harmful results.

Cadmium Platings and Coatings.—The use of cadmium for plating purposes is growing in popularity and was first applied to the waterproofing of piano wires, then to motor parts and accessories. It is used as a substitute for silver on ornamental articles and for nickel and chromium in other industries. Cadmium plating is best carried out in cyanide baths although acid solutions of the chloride or sulphate are also used. A. Siemens (Z. Elektrochem. 1930, **36**, 101) recommends in cyanide baths a 10% excess of cyanide over that needed to form $K_2Cd(CN)_4$. The cadmium content of the solution is 40–50 g. per litre, the process being carried out at 40°. The throwing power of these baths is so good that articles of complicated design may be plated. The efficiency is 93–98%, a coating 5μ thick being produced in 15 minutes with a cathode current density of 1 amp. per sq. dm. The addition of small quantities of colloids, and of copper, nickel, or cobalt compounds is said to aid the formation of good deposits. F. Pietrafesa and C. Luciani (Met. Ital. 1932, **24**, 1) suggest sodium-cadmium baths. Increase in cadmium concentration gives increase in cathodic yield and in grain size. Increase in free $NaCN$, $NaOH$, or Na_2CO_3 increases the efficiency of the bath but reduces adhesion. Gelatin is found to be the best colloid for refining the grain size, but if this be used the presence of tin, lead, or antimony in the bath is deleterious. A zinc-cadmium brass (Cu 60–63, Zn 16–18, Cd 20–23%) may be deposited from cyanide baths; variations in the composition of the deposit may be effected by varying the composition of the bath, the current density used, the temperature of the bath, or the rate of agitation. Ternary alloys of zinc, cadmium and antimony may be electro-deposited from solutions containing zinc and cadmium as cyanides, and antimony as potassium antimonyl tartrate. A high cadmium concentration is required for an appreciable percentage of cadmium in the deposit.

Cadmium coating may be effected by spraying the molten metal on to the object to be treated, and such coatings are stated to be superior to zinc in protecting petrol storage tanks from corrosion (Pessel, Ind. Eng. Chem. 1930, **22**, 119). Cadmium affords better protection to iron and steel than does zinc against corrosion by the salt spray test and also in a warm, damp atmosphere and even if the coating be pierced the underlying metal is still protected. Against industrial atmospheres zinc is better than cadmium (*cf.* G. W. Blum, Metal Progr. 1936, **29**, 40). Cadmium coatings are superior to zinc as a protection against sea-water, but they are corroded by acetic, tartaric, citric and lactic acids, and by acid foodstuffs such as vinegar, cider and fruit acids, giving cadmium salts in quantities toxic to human beings.

Compounds of Cadmium.—*Cadmium Monoxide*, CdO, is prepared by heating the carbonate, nitrate or hydroxide, or by burning the metal in a current of air or oxygen. It has also been obtained by heating cadmium in contact with the vapour of water, although if steam be passed over the heated metal the latter volatilises below the temperature of reaction. This oxide is also formed by the action of sodium peroxide on molten cadmium, by the calcination of cadmium oxalate, by heating a mixture of cadmium chloride and mercuric oxide, or by melting cadmium fluoride with alkali carbonate. As usually prepared and met with, it is a dark brown refractory powder, and if this powder be heated in a current of oxygen it forms a dark red crystalline mass. It volatilises in air free from reducing agents at 700° as compared with the volatilisation of zinc oxide at 1,000°. It is insoluble in water but soluble in acids. It absorbs carbon dioxide from the atmosphere and is readily reduced to metal by carbon or carbon monoxide. Its reduction by solid carbon commences at about 600°. It is used in alkaline accumulators. When finely ground with water (with or without zirconium silicate), moulded into shape, and heated to 800° it forms a mass of high tensile strength which is used for resistors in electric furnaces, and these are stable at high temperatures and more durable than the usual metal resistors. It becomes conducting when heated and therefore requires an auxiliary heating circuit (U.S.P. 1467810, 1923).

Cadmium Hydroxide, $Cd(OH)_2$, is a white amorphous powder precipitated by the action of alkalis on solutions of cadmium salts. It is soluble in ammonia but insoluble in solutions of sodium or potassium hydroxide or ammonium carbonate. It loses the elements of water at 300°.

Cadmium Suboxide, Cd_2O, is formed when cadmium oxalate is heated in a stream of carbon dioxide (Tanatar, Z. anorg. Chem. 1901, **27**, 433), or when cadmium oxide is heated with carbon monoxide (Brislee, J.C.S. 1908, **93**, 162). It may also be prepared by dehydrating cadmous hydroxide, obtained by the action of water on the product formed by fusing cadmium chloride with metallic cadmium (Morse and Jones, J. Amer. Chem. Soc. 1890, **12**, 488; *cf.* Denham, J.C.S. 1919, **115**, 556).

Cadmium Peroxide.—Haas prepared the peroxide with a composition ranging from Cd_5O_8 to Cd_3O_5 (Ber. 1884, **17**, 2249), while more recently Perkins has prepared peroxides corresponding to the formulæ Cd_3O_5,xH_2O, $Cd_4O_7,2H_2O$, and $3CdO,2H_2O_2$; cadmium oxide can be peroxidised by ozone at ordinary temperatures (J.C.S. 1929, 1687).

Cadmium Chloride, $CdCl_2$, is prepared by evaporating the solution of the metal or oxide in hydrochloric acid. It melts below a red heat and sublimes at a higher temperature, condensing in the form of micaceous plates. The hydrated chloride separates from a solution as $CdCl_2,2\frac{1}{2}H_2O$.

Cadmium Iodide, CdI_2, is obtained by digesting 1 part of cadmium with 2 parts of iodine in water and evaporating. It crystallises in large transparent tables soluble in water and alcohol. It is now seldom used in medicine. On account of its stability and solubility in alcohol has been used for iodising collodion plates in photography

Cadmium Sulphide, Cadmium Yellow, Jaune Brillant, CdS. — Occurs in the mineral greenockite. This compound may be prepared by the action of hydrogen sulphide on a solution of a cadmium salt or on cadmium vapour or by heating cadmium or preferably cadmium oxide with excess of sulphur. It has also been produced electrolytically in a two-compartment cell Sticks of electrolytic cadmium were used as anode and steel as cathode, and a weak acid solution of an alkali sulphide as electrolyte. Ferrous sulphide dissolved in the cathode compartment acted as the source of sulphur, the iron remaining in a finely divided state as a by-product The cadmium sulphide was precipitated in the anode compartment (C G. Fink and W. M. Grosvenor, Jnr, Trans. Amer. Electro chem. Soc. 1930, 58, 475). That prepared by the first method has the best colour and covering power. The various hues of different preparations depend on whether the substance is crystalline or amorphous, and on the size and nature of the surface of the grains It may be lemon yellow or orange red in colour, and when heated to redness it becomes first brown and then carmine. It melts at 1,750° under 100 atmospheres pressure and solidifies on cooling, in laminæ of the original colour It is decomposed by roasting and is soluble in concentrated hydrochloric acid, it is also soluble in nitric acid, and with difficulty in sulphuric acid. Cadmium sulphide has a brilliant colour and is used as an oil and a water colour, and especially in the pottery trade. It is used for colouring soaps and in calico printing, also for colouring rubber articles, in which it has no adverse effects on the properties and is supposed to assist vulcanising; it is also used for the production of a blue flame in pyrotechny. It is made into enamel pigments by adding alkaline or alkaline earth sulphides to a solution of a cadmium salt and igniting the product. The colours range from bluish red to orange-red. In association with selenium, red pigments known as *cadmium red* are obtained by heating 80–90 parts of cadmium sulphate with 20–10 parts of selenium, the product consisting of a mixture of crystals of sulphide and selenide of cadmium. Cadmium sulphide, on account of its cost, is very seldom used alone, but is mixed or adulterated with other pigments. Pigments composed of sulphide carbonate mixtures or sulphide selenide mixtures are most prominent. The *cadmopones* which are suitable for use as industrial pigments consist of cadmium sulphide or sulphide-selenide mixtures co precipitated with barium sulphate; these, although more expensive than lithopone, have a better colour and a greater covering power. Zinc-base pigments are the chief adulterants used; adulteration with copper or lead-base pigments results in double decomposition and blackening, owing to the formation of black sulphide of copper or lead. Cadmium sulphide is often used as a final coat over several coats of chrome yellow.

Cadmium Sulphate, $CdSO_4$, is a very soluble salt prepared by dissolving the oxide or carbonate in sulphuric acid. The hydrous salt $3CdSO_4,8H_2O$, is the principal form met with. It loses its water at 170° and its SO_3 at 890°. It is used to some extent in medicine in place of zinc sulphate, especially on the Continent. It is also used in the construction of the Weston normal cell as a standard of E.M.F. The cell is usually made in the form of an H. One of the limbs contains mercury covered by a paste of mercurous sulphate, the other contains cadmium amalgam. Above both, to nearly the top of the limbs, which are closed by waxed corks, is a saturated solution, with crystals of cadmium sulphate. Through the glass of the lower limbs platinum wires pass. The cell has an E.M.F. of 1 0183 volts at 20°, and has the advantage of a very low temperature coefficient, falling by 0 00004 volt for a temperature rise of 1°. Cadmium sulphate forms double salts with ammonium sulphate; one such salt has the formula

$$CdSO_4 \cdot (NH_4)_2SO_4, 6H_2O,$$

and another salt having the formula

$$2CdSO_4 \cdot (NH_4)_2SO_4$$

consists of microscopical crystals, hygroscopic, yellow when hot, white when cold, and has d^{22} 3 11 (Veres, Compt. rend. 1914, 158, 39).

Cadmium Nitrate, $Cd(NO_3)_2,4H_2O$, is prepared by dissolving the oxide or carbonate in nitric acid It crystallises in deliquescent fibrous needles, soluble in alcohol. Cadmium nitrate is used as a colour for glass and porcelain in the ceramic industry.

Cadmium Cyanide, $Cd(CN)_2$, is obtained as a white precipitate when potassium or sodium cyanide is added to a fairly concentrated solution of a cadmium salt. It dissolves in excess of KCN or NaCN, and this solution is used as the electrolyte for electro deposition of cadmium.

Cadmium Salicylate is prepared from the acid and the oxide or carbonate. It is readily soluble in alcohol, ether or glycerol, and is used in medicine as an external antiseptic. C. O. B.

CADMIUM LITHOPONE. A yellow pigment in which cadmium sulphide replaces the zinc sulphide of ordinary lithopone

$$(ZnS+BaSO_4),$$

or a mixture of cadmium sulphide and barium sulphate precipitated together.

CADMIUM ORANGE, CADMIUM RED. A mixture of cadmium sulphide and cadmium selenide in varying proportions together with barium sulphate. The colour range is from red to purple (*cf.* J. Amer. Ceram. Soc. 1930, 13, No. 5, ii, 44, and G.P. 337992 of 4/9/19 with addition 388535 of 31/1/20).

CADMIUM YELLOW. The pigment consists of cadmium sulphide, which exists in two modifications, lemon yellow and orange red; the commercial pigment varies in shade within these limits

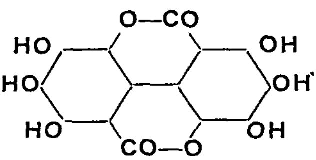
CAERULEOELLAGIC ACID, $C_{14}H_6O_{10}$, is prepared by heating ellagic or flavellagic acid

with sulphuric acid (monohydrate) at 185°–200°, or with arsenic and sulphuric acids at 100°–130° (Perkin, J.C.S. 1911, **99**, 1442). It crystallises from pyridine in small pale yellow prismatic needles which melt above 360° and are very sparingly soluble in the usual solvents. Concentrated solutions of the alkali hydroxides dissolve it with a greenish-yellow colour which, on dilution, becomes green and finally blue ; these changes appear to arise from oxidation. On distillation with zinc dust fluorene is produced.

The *hexa-acetyl* derivative, colourless needles, m.p. 330°–332°, and the *hexabenzoyl* compound, colourless needles, m.p. 343°–345°, have been prepared.

When digested with aqueous-alcoholic potassium hydroxide, caeruleoellagic acid yields *octahydroxydiphenyl*, an almost colourless crystalline powder, soluble in dilute potassium hydroxide with a reddish-violet colour which becomes brown on exposure to air. The *octa-acetyl* derivative, colourless needles, melts at 177°–178°.

The following constitution is therefore assigned to caeruleoellagic acid :



Caeruleoellagic acid possesses well-marked dyeing properties and yields the following shades on mordanted woollen cloth :

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Deep olive-yellow.	Greenish-yellow.	Dull yellow.	Greenish-black.

A. G. P. and E. J. C.

CÆRULEUM MONTANUM *v.* AZURITE.

CÆSALPINA SAPPAN (Fam. Leguminosæ). An Indian tree, the wood of which, used as an astringent in place of logwood, contains brazilin. The drug is known as *sappan.*

CÆSIUM. Sym. Cs. At. wt. 132·91, at. no. 55, no isotopes.

History.—The discovery of the element cæsium was hastened by the use of the spectroscope. In 1846 C. F. Plattner (Pogg. Ann. 1846, **99**, 443) analysed the mineral pollucite from the Isle of Elba and was mystified on finding that the constituents determined totalled only 92·75% ; careful search did not reveal any error in analysis or the omission of any constituent. In 1860 R. Bunsen and G. Kirchhoff (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1860, 221) using the recently devised spectroscope to examine the mineral constituents of the spring waters of Dürkheim, observed two lines of unknown origin; these they attributed to a new alkali metal, for which they proposed the name cæsium, from the Latin *cæsius* for blue as of blue eyes ; this was the first element to be detected by the spectroscope, and for the investigation of the compounds of the elements found in this water 40 tons were evaporated. In 1864 F. Pisani (Compt. rend. 1864, **58**, 714) repeated the analysis of the mineral pollucite and found that the whole of the potassium and part of the sodium reported by Plattner should have been determined as cæsium, which would account for the 7·25% missing in the analysis.

Occurrence.—Minerals containing cæsium are widely distributed in nature, but there are few deposits rich enough to furnish large supplies of the metal. Most of the minerals containing cæsium contain the elements rubidium and lithium also. *Lepidolite* (*q.v.*) is one of the best known lithium- and rubidium-bearing minerals; it is a complex lithia mica and has been found to contain as much as 0·77% Cs_2O. *Petalite*, $Li_2O,Al_2O_3,8SiO_2$; *amblygonite*, $2LiF, Al_2O_3,P_2O_5$; *triphylite* ($LiFePO_4$ with some Mn) ; *lithiophilite* ($LiMnPO_4$ with some Fe), and *carnallite*, $KCl,MgCl_2,6H_2O$, may contain small quantities of cæsium in addition to considerable quantities of Li_2O. Cæsium occurs free from rubidium and lithium in the rare mineral *pollucite* or *pollux* from Elba and Hebron (Maine) ; this mineral is a hydrated cæsium alumino-silicate in which the alumina is associated with ferric oxide, it may contain up to 32% Cs_2O. (For treatment, *see* A. Kastler, Bull. Soc. chim. 1927, [iv], **41**, 428.) Cæsium is also found in the mineral waters of Frankenhausen, Baden-Baden, Vichy, and the Wheal Clifford Spring; 1 litre of the latter was found to contain 1·71 mg. by T. Yorke (J.C.S. 1872, **25**, 273). It occurs in the waters of Bourbonne-les-Bains to the extent of 32·5 mg. of CsCl per litre. Cæsium has also been found in notable quantities in the products of the eruption of Vesuvius (F. Zambonini and L. Coniglio, Atti R. Accad. Lincei, 1926, [vi], **3**, 521). It is also found in sea-water and in the ashes of plants.

Separation.—*See* CHEMICAL ANALYSIS (p. 585).

Preparation.—Cæsium metal may be prepared by the electrolysis of a fused mixture of cæsium cyanide 4 parts, and barium cyanide 1 part, using electrodes of aluminium (Setterberg, Annalen, 1882, **211**, 100). It was obtained by N. W. Beketoff by heating the hydroxide with aluminium in a nickel retort and condensing the metal in a glass receiver (J. Russ. Phys. Chem. Soc. 1888, **20**, 363). The metal was also obtained by Erdmann and Menke (J. Amer. Chem. Soc. 1899, **21**, 259) by heating a mixture of cæsium carbonate and metallic magnesium, and a similar method for the reduction of cæsium hydroxide was used by E. Graefe and M. Eckardt (Z. anorg. Chem. 1899, **22**, 158). A more rapid method giving a better yield is reduction by calcium ; 1 part of calcium in small pieces together with 4 parts of cæsium chloride are heated in an exhausted hard glass tube ; reduction takes place at about 400°, when the cæsium volatilises and condenses in the cooler part of the tube (L. Hackspill, Ann. Chim. Phys. 1913, [viii], **28**, 613). R. E. Miesse has more recently patented a process for the preparation of the metal by heating cæsium chloride and a rare metal alloy to 270° in an exhausted glass vessel until all traces of gas are removed. The mixture is then more strongly heated by radiation from an electric heater until reaction takes

place with the production of cæsium metal and rare earth chlorides (U.S.P. 1707637, 1929).

Detection and Estimation.—See CHEMICAL ANALYSIS (pp. 566, 585)

Spectrography—The more persistent lines obtained with cæsium chloride solutions, using a spark method, are 4,593 2, 4,555 3, 4,538 9, and 2,525 6 (Twyman, "Wave Length Tables," A. Hilger, London, 1931). A de Gramont, also using spark methods, states that the distinctive lines are 4,593 2 and 4,555 3 H. Lundegarth confirms these figures but recommends a flame spectrum technique and claims that the line 4,593 2 will detect 0 0005 mol per litre ("Die Qualitative Spektranalyse der Elemente," Jena, 1929).

Properties.—Cæsium is a silvery-white metal resembling rubidium and potassium in appearance. Its space lattice is body centred cubic and the size of unit cell is 6 05 Å. It is soft enough to be cut with a knife, tarnishes rapidly in air, and decomposes water at ordinary temperatures The action on water can be detected at $-116°$, it may be preserved in petroleum Its sp gr. at 0° is 1 9029 (L Hackspill, Compt. rend. 1911, 152, 259), its melting-point is 28 45° (E. Rengade, Compt. rend. 1913, 156, 1897), and its boiling point 670°. It burns with a reddish violet flame. The heat of fusion is 3 766 g cal, the specific heat of the solid metal is $0\,0522+0\,00013t$ and of the liquid metal $0\,0604+0\,000034t$, the atomic heat at 0° is 6 95 (Rengade, *l c*) The coefficient of expansion of the solid metal is 0 000291 and of the liquid metal up to 50° is 0 000345 (Hackspill, *l c*). It is the most electro positive of the elements. Its salts are stable and it has a strong tendency to form double salts. The salts are isomorphous with those of potassium and rubidium. E. Rinck (Compt. rend. 1934, 199, 1217) has determined the equilibrium diagram of the cæsium sodium alloys by thermal analysis. A eutectic point occurs with 75 at. % Cs at $-30°$ and a transition point with 71 at. % at $-8°$, a compound Na_2Cs being deposited between these points

Uses.—There is little demand for cæsium, but it appears on the market as salts, mainly chloride and hydroxide, and only rarely in the metallic form. It has been used in the manufacture of radio-valves, cæsium chloride is mixed with magnesium and calcium and compressed into small pellets which are introduced into the tubes The pellets are flashed, eliminating the last traces of air and thus securing the desired vacuum. The cæsium chloride supplies positive ions at the filament. Cæsium is employed to a certain extent in the manufacture of photo electric cells, where it is present as a molecular layer on the silver or base metal electrode. The photo emission of the thin cæsium layer is greater than that of the massive metal. It is employed also in certain luminous tubes containing neon under reduced pressure; the electrodes are mainly of graphite and contain occluded cæsium vapour. Cæsium is found to promote the catalytic action of iron in the synthetic ammonia processes (U.S.P. 1510598).

Compounds.—*Cæsium hydroxide*, $CsOH$, is greyish white in colour, fuses readily at a red heat and crystallises from the fused mass in opaque brittle crystals. Its sp gr. is 4 018. It is very hygroscopic and dissolves in water with great evolution of heat due to the formation of hydrates and also to ionisation. *Cæsium monoxide*, Cs_2O, is prepared as an orange-red powder by burning cæsium in insufficient oxygen for its complete oxidation and distilling off the excess metal; it may also be prepared by shaking a solution of cæsium in liquid ammonia with oxygen, when a pale pink precipitate of Cs_2O is obtained. *Cæsium peroxide*, CsO_2, is formed by heating cæsium to 300° in excess of oxygen (Rengade). On heating CsO_2 or on heating cæsium in the theoretical amount of oxygen the *oxide* Cs_2O_3 is formed. *Cæsium hydride*, CsH, is obtained as a white crystalline compound on heating the metal in hydrogen at 300°. It is liable to ignite in a damp atmosphere and decomposes into metal and hydrogen on heating to 500°. It is coloured by exposure to cathode rays (Rengade). *Cæsium sulphate*, Cs_2SO_4, has properties similar to those of the alkali sulphates. It forms alums with the sulphates of the trivalent elements. It may be used for the detection of aluminium; when its solution is added to a solution of an aluminium salt a copious precipitate of the insoluble alum, $Cs_2SO_4\,Al_2(SO_4)_3{,}24H_2O$, comes down (Hart and Huselton, J. Amer. Chem. Soc. 1914, 36, 2082) This test is sensitive to 0 1 mg per c c. Al, and only bismuth interferes *Cæsium chloride*, $CsCl$, melts at 626°. It volatilises at high temperatures without decomposition. At 2,000° the vapours are composed of simple molecules. It boils at 1,303° under 760 mm. pressure The percentage contraction of cæsium halides on formation is very high and is equal to 54 9% with $CsCl$. The property of forming polyhalides is connected with the volume of the cation, so that cæsium with the largest atomic volume forms them readily, and CsI_3, CsI_5, and CsI_9 are known, also $CsBr_3$ and $CsBr_5$, but no polychlorides. There are, however, a considerable number of polyhalides containing different halogens such as $CsIBr_2$, $CsICl_2$, $CsBrCl_2$, $CsClBr_2$. The colour gradates from the black of polyiodide through orange to a pale yellow in the bromochlorides. CsI_3 is so stable that it has a decomposition pressure of only one atmosphere at 250°. When a polyhalide is exposed to air or is heated it becomes white and the simplest alkali halide containing the most negative of the halogen atoms is left behind.

C. O. B.

CAFFEARINE. Found in the mother liquors of caffeine from coffee berries. It is identical with trigonelline (v. BETAINES) (Gorter, Annalen, 1910, 372, 237).

CAFFEIC ACID, 3:4-dihydroxycinnamic acid, $C_6H_3(OH)_2CH{:}CH{\cdot}COOH$, crystallises anhydrous in yellow prisms from concentrated aqueous solution, but with 1 mol. H_2O from the dilute solution. It is found in coffee beans, also in the resin of *Pinus laricio*, in hemlock, and in the bark of *Cinchona cuprea*. Coffee beans contain chlorogenic acid, which splits up into caffeic acid and quinic acid. The melting-point recorded ranges from 195° (Bamberger and

Klimburg, Monatsh. 1917, **38**, 462) to 223°–225° (Power and Browning, J.C.S. 1914, **105**, 1832). For percentage of the acid in natural and treated coffee, *v.* Rinck and Kaempf (Pharm. Zentr. 1931, **27**, 690). For detection, *v.* Hoepfner (Chem.-Ztg. 1932, **56**, 991). For estimation, *v.* Plücker and Keilholz (Z. Unters. Lebensm. 1933, **66**, 200, 615 ; 1934, **68**, 97 ; Chem.-Ztg. 1934, **58**, 542). J. N. G.

CAFFEINE AND THE ALKALOIDS OF TEA, COFFEE, AND COCOA.—The alkaloids of tea, coffee, cocoa and similar stimulant foodstuffs constitute a group of closely related derivatives of purine, $C_5H_4N_4$ (VIII). The most important of these are caffeine, theobromine, and theophylline, all of which are used in medicine. The structural relationships of these alkaloids are shown below. Xanthine, hypoxanthine, and adenine have also been found in small amounts in tea.

Caffeine, $C_8H_{10}O_2N_4$, *1:3:7-trimethylxanthine* (VII), is the most important alkaloid of the group and is found in tea, coffee, kola nuts, *maté*, and guarana paste in amounts varying from 1 to 5% either free or combined with chlorogenic acid. Caffeine is obtained from tea waste and tea dust, and also as a by-product in the production of caffeine-free coffee. It is prepared synthetically in large quantities from theobromine by methylation with dimethyl sulphate in alkaline solution, a method which has largely displaced the older synthetic process from uric acid.

For the production of caffeine from tea dust and similar products the material is mixed with lime and extracted with water, the extract concentrated, treated with litharge or magnesia, filtered, the filtrate concentrated and allowed to crystallise. Purification is effected by recrystallisation from water.

In the preparation of caffeine-free coffee the beans are first treated with super-heated steam and then extracted with a suitable low boiling solvent such as benzene or ethylidene chloride. The solvent is recovered and the residual crude caffeine purified by crystallisation from water.

Caffeine is very soluble (1 in 1) in boiling water, from which it crystallises on cooling, with one molecule of water. It is readily soluble in alcohol and in chloroform, less soluble in benzene and ether. The anhydrous base has m.p. 234°–235° and sublimes at about 175°. It is a weak base and its salts dissociate on evaporation of their aqueous solutions. In common with the other alkaloids of this series caffeine gives the murexide reaction. A few crystals evaporated to dryness with a few drops of hydrochloric acid and a crystal of potassium chlorate give a brilliant purple colour on addition of ammonia. The colour is discharged by sodium hydroxide. Caffeine is official in the British Pharmacopœia and is very widely used in medicine, either in the form of the free base or as the citrate. Caffeine is a cardiac and renal stimulant and acts on the central nervous system, increasing mental activity, and in admixture with acetanilide, acetylsalicylic acid, or phenacetin is employed for the relief of nervous headache and migraine. Combinations of caffeine with sodium benzoate or sodium salicylate, on account of their greater solubility, are used for injections.

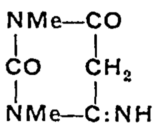
Theobromine, $C_7H_8O_2N_4$, 3:7-dimethylxanthine (VI), is the principal alkaloid found in cocoa beans, in which it occurs to the extent of from 1·5 to 2%. It is found also in small quantities in kola nuts and leaves, in guarana, and in tea.

For the preparation of theobromine, the husks of the cocoa bean containing from 0·5 to 1% of theobromine are freed from fat as far as possible either by pressure or by extraction with light petroleum and the residue extracted with benzene or toluene. After removal of the solvent, the residue is purified by crystallisation from water or alcohol or by solution in alkali and reprecipitation by acid. Other methods depend on extraction with milk of lime and precipitation of the theobromine by addition of hydrochloric acid to the solution so obtained.

Theobromine is a white crystalline powder, m.p. 351°, and sublimes at about 290°. It is sparingly soluble in water and most organic solvents, but crystallises well from glacial acetic acid. It is amphoteric but rather more basic than caffeine, although its salts with acids dissociate in water. It also forms salts with bases and the calcium salt can be crystallised from water.

Theobromine is largely used in medicine, principally for its diuretic action. It resembles caffeine in its effects, its action on the central nervous system being, however, much less marked, and its renal effect more pronounced. It is employed alone or in combination with sodium acetate or sodium benzoate, etc. A mixture with sodium salicylate is official in the British Pharmacopœia.

Theophylline, $C_7H_8O_2N_4$, 1:3-dimethylxanthine (V) is isomeric with theobromine, and is found in small amounts in tea. Technically it is prepared synthetically from dimethylcarbamide and ethyl cyanacetate (Traube, Ber. 1900, **33**, 3035). Condensation by means of phosphoryl chloride gives 1:3-dimethyl-4-iminobarbituric acid (I). Nitrous acid converts this to the oximino derivative (II), which on reduction gives dimethyl-diamino-dioxy pyrimidine (III). This on treatment with formic acid yields the formyl derivative (IV), which on heating loses water with formation of theophylline (V). The constitution of theobromine (VI), caffeine (VII), and purine (VIII), is also shown.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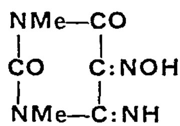
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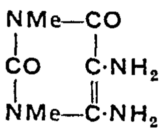
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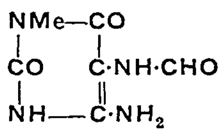
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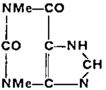

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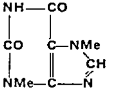

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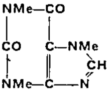
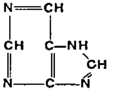


VII.



VIII.

Theophylline crystallises with $1H_2O$, m.p. 269°–272°. It is sparingly soluble in water but readily soluble in solutions of alkali hydroxides. It is a weak base and yields salts with acids. It also forms derivatives with metals. Theophylline is employed in medicine, having a more marked diuretic action than theobromine. Theophylline sodium acetate, an equimolecular mixture of the two components, is soluble in water (1–25) and is official in many pharmacopœias

Adenine, $C_5H_5N_5$, 6 amino-purine, m.p. 360°–365°, sublimes at 250°, and is sparingly soluble in water. Hypoxanthine, $C_5H_4ON_4$, 6 oxypurine, m p. 150°, and xanthine, $C_5H_4O_2N_4$, 2 6-dioxy-purine have, like adenine, been found in small quantities in tea but are of no technical importance. Purine has not been found occurring naturally but was synthesised by Fischer (Ber. 1898, 31, 2550). A. J. E.

CAFFEOL, *caffeone*, the name given to an oil obtained by steam distillation of roasted coffee beans and extraction of the distillate with ether (Erdmann, Ber. 1902, 35, 1846) It contained acetic acid, valerianic acid, and furfuryl alcohol. The characteristic aroma was due to a nitrogenous substance, which decomposed when distilled, giving off an odour of pyridine (Bertrand and Weisweiller, Compt. rend. 1913, 157, 212) The B P. 246454 of the Internationale Nahrungs- und Genussmittel A.-G. modified the process by employing a high vacuum and in the most volatile fraction detected diacetyl and other aliphatic α diketones, acetaldehyde and methylethylacetaldehyde (2 methylbutaldehyde). The less volatile fraction forms a yellow or brown oil which is intended for flavouring foodstuffs.

CAFFETANNIC ACID consists mainly of chlorogenic acid.

CAIL-CEDRA. *Khaya senegalensis* A. Juss. A tree of the meliaceous order, growing on the banks of the Gambia and on the lowlands of the peninsula of Cape de Verde. Its bark is very bitter, and is much prized by the natives as a febrifuge, on which account it has been called the *cinchona of Senegal*; it contains, amongst other substances, an extremely bitter, neutral resinous substance, called cail cedrin, to which its active properties appear to be due.

One kilogram of the bark yields about 8 mg. of cail cedrin (Caventou, J. Pharm. 1849, [iii], 16, 355 ; 1858, 33, 123).

CAIRNGORM. A variety of quartz of a brownish colour.

CAJUPUT, ESSENTIAL OIL OF.—The oil distilled from the fresh leaves and twigs of *Melaleuca leucadendron*, Linn. (Fam. Myrtaceæ). The shrub is found in India, the Malay Peninsula, the Dutch East Indies, the Molucca Islands, and in Northern Australia. A large number of species of *Melaleuca* are found in Australia, where they are known as tea trees, and the oils have been found to vary considerably in composition. The crude oil is obtained chiefly from the East Indies and is imported in wine bottles. It is generally bluish or green in colour owing to the presence of copper derived from the still. For medicinal purposes it is required to be redistilled.

Composition.—The chief constituent is cineole, of which it contains 50–65%. It also contains *l*-α-pinene, a sesquiterpene, benzaldehyde and terpineol combined with acetic, butyric and valeric acids.

Characters.—It is a colourless or yellow oil, sp gr. 0 916–0 926 at 15 5°, $[\alpha]_D^{20}$ 0° to −4°, n_D^{20} 1 462–1 472. Soluble in 2 vols. of 80% alcohol. The cineole is determined by the method official in the British Pharmacopœia

Cajuput oil is used medicinally as a carminative, as an anti-spasmodic, and as an intestinal antiseptic. It is also used externally in rheumatic affections. C. T. B

CAJUPUTOL, $C_{10}H_{18}O$, eucalyptol (B P.C. 1934).

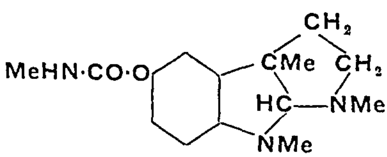
CAL. Cornish name of wolfram (ferrous manganese tungstate) $FeMnWO_4$.

CALABAR BEAN (Fr. *Fève de Calabar*, Ger. *Gottesgerichtsbohne*) is the seed of *Physostigma venenosum* Balfour, a woody climber related to the scarlet runner (Fam. Leguminosæ). The bean was first made known in Britain by Daniell (Edinburgh New Philos. J. 1846, 40, 319) who described how among certain West African tribes prisoners convicted of a capital offence were made to swallow a potion prepared from the bean, which is hence also called *Ordeal Bean* ; it is further known by its native name of *Eseré* or *chopping nut*. The plant grows near the mouths of the Niger and Old Calabar rivers ; the beans measure 25×18×12 mm , are oblong reniform and of a dark chocolate-brown ; their physiological properties were examined at Edinburgh by Christison and by Fraser, and the drug was introduced into medicine by Argyll Robertson, on account of its miotic properties. The last two investigators already observed that the action of the drug is antagonised by belladonna (1863). Jobst and Hesse (Annalen, 1864, 129, 115) traced the action to an amorphous alkaloid *physostigmine*, whilst Vée and Leven, in a note of a few sentences (Compt. rend. 1865, 60, 1194), mentioned that the alkaloid was "crystallisable" ; they termed it *eserine* (from the native name for the bean), but gave little detail. The name physostigmine seems preferable on grounds of priority ; yet both synonyms are in use. Hesse established the formula

$C_{15}H_{21}O_2N_3$ for the alkaloid, which is best prepared by shaking with ether, in presence of an excess of sodium carbonate, the water-soluble portion of an alcoholic extract of the beans. The ethereal extract is then shaken with very dilute sulphuric acid until the acid is neutralised by the alkaloid, and from this solution physostigmine is precipitated as the salicylate. Several related alkaloids are present in small amount; the total alkaloid in the bean is 0·05–0·3%; it may be estimated according to Salway (Amer. J. Pharm. 1912, **84**, 49), who employs ether, sodium carbonate, and titration with iodeosin as indicator.

Physostigmine crystallises in two forms, m.p. 86°–87° and m.p. 105°–106°; the latter is the more stable and is formed on spontaneous evaporation of a solution in benzene. It is soluble in alcohol, ether and chloroform, somewhat so in water to an alkaline solution; $[\alpha]_D$ −75·8° (in chloroform). The *salicylate* (B.P., U.S.P.) is the principal salt; 1 g. dissolves at 25° in 75 c.c. of water, 16 c.c. of alcohol, 6 c.c. of chloroform, 250 c.c. of ether; at 80° in 16 c.c. of water; in 5 c.c of boiling alcohol. It forms colourless acicular crystals, $B{\cdot}C_7H_6O_3$, m.p. 186°–187°. The *sulphate*, $B_2{\cdot}H_2SO_4$, m.p. 145°, is a microcrystalline, deliquescent powder and is no longer in the British Pharmacopœia. The *hydrobromide*, $B{\cdot}2HBr$, m.p. 224°–226° (from alcohol); the *aurichloride*, $B{\cdot}2HAuCl_4$, m.p. 163°–165°; the *platinichloride*, $B{\cdot}H_2PtCl_6$, m.p. 180°; the *mercuri-iodide*, $B{\cdot}HI{\cdot}HgI_2$, m.p. 170°; the *benzoate*, $B{\cdot}C_7H_6O_2$, m.p. 115°–116° (from ether); and the *picrate*, m.p. 114°, can all be crystallised. The sulphate and the benzoate each dissolves in about 4 parts of water at room temperature, and are therefore much more soluble than the salicylate. On exposure to air, solutions of physostigmine salts slowly acquire a pink colour; on addition of sodium hydroxide a white precipitate is formed, which soon turns pink, and dissolves in excess of the alkali with a red colour. This is caused by hydrolysis to the very unstable phenol *eseroline*, which is oxidised by air to *rubreserine* (*see below*). Physostigmine dissolves in nitric acid with a yellow colour which becomes red on warming and leaves on evaporation a green residue. On evaporation with excess of ammonia, a red solution is formed and ultimately a blue residue is left.

The constitution of physostigmine has been chiefly elucidated by Polonovski and his collaborators (1893–1924), further by Salway (J.C.S. 1912, **101**, 978), Straus (Annalen, 1913, **401**, 350; 1914, **406**, 332), Barger and Stedman (J.C.S. 1923, **123**, 758), Stedman (*ibid.* 1924, **125**, 1373). The subjoined constitution

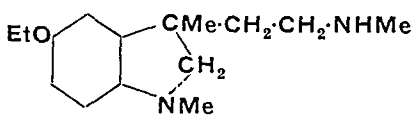


was suggested by Stedman and Barger (J.C.S. 1925, **127**, 247) and has been confirmed by synthesis (Julian and Pikl, J. Amer. Chem. Soc. 1935, **57**, 755; *see also* King, Liguori, and Robinson, J.C.S. 1934, 1416; King and Robinson, *ibid.* 1935, 755; Hoshino and Kobayashi, Annalen, 1935, **520**, 11). On hydrolysis with alkali methylamine, carbon dioxide and *eseroline*, $C_{13}H_{18}ON_2$, are formed (Petit and Polonovski, Bull. Soc. chim. 1893, [iii], **9**, 1008). Physostigmine is thus the methyl urethane of eseroline, and its partial synthesis from eseroline and methyl carbimide, CONMe, was effected by Polonovski and Nitzberg (*ibid.* 1916, [iv], **19**, 27). Eseroline is readily oxidised on exposure to air, and ultimately forms *rubreserine* (Ehrenberg, Verh. Ges. deut. Naturforsch. Aertze, 1893, II, 102), according to the equation:

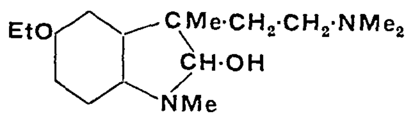
$$C_{13}H_{18}ON_2 + O_2 = C_{13}H_{16}O_2N_2, H_2O$$

Rubreserine crystallises from water in deep red needles, m.p. 152° (anhydrous). Under certain conditions the oxidation may proceed to *eserine blue*, $C_{17}H_{23}O_2N_3$, which appears to be a combination of eseroline with an oxidation product (Salway, *l.c.*). The constitution of these colouring matters has not been elucidated. Eseroline contains two *N*-methyl groups and forms a monomethiodide; on heating the latter in an atmosphere of carbon dioxide, a hydroxyindole, *physostigmol*, $C_{10}H_{11}ON$, is formed (Straus).

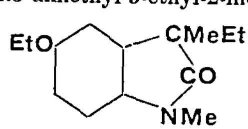
By the synthesis of its ethyl ether, Stedman (*l.c.*) showed physostigmol to be 5-hydroxy-1:3-dimethylindole. Straus, and also Polonovski, considered that the pyrrole ring is fused to a piperidine nucleus, but Stedman and Barger (*l.c.*) showed by exhaustive methylation of eseroline ethyl ether or *eserethole* that the remaining ring is a pyrrolidine nucleus and that there is a C-methyl group attached to a pyrroline ring. Reduction of eserethole by zinc and hydrochloric acid (Polonovski, Bull. Soc. chim. 1918, [iv], **23**, 357) or catalytically (Stedman and Barger) opens the pyrrolidine ring with formation of the secondary base dihydro-eserethole.



The pseudo base eserethole methine



is reconverted by hydriodic acid with ring closure into eserethole methiodide; on oxidation with ferricyanide the secondary alcohol is converted into a ketone which by exhaustive methylation loses trimethylamine and can then be reduced to 5-ethoxy-1:3-dimethyl-3-ethyl-2-indolinone,



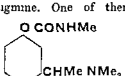
Calabar beans contain a number of subsidiary alkaloids in small quantity. *Geneserine* (Polo-

novski and Nitzberg, Bull. Soc. chim. 1915, [iv], **17**, 244, 290; 1916, [iv], **19**, 27; Polonovski, *ibid.* 1917, [iv], 21) has the composition $C_{15}H_{21}O_3N_3$, and was obtained by extracting the beans, previously soaked in 2% sodium hydroxide solution, with ether. It forms orthogonal crystals, m p. 128°–129°, $[\alpha]_D$ −175° (in alcohol). It is a weak base, does not form crystalline salts with mineral acids, but yields a salicylate, m p. 89°–90°, a picrate, m.p. 175°, and a methiodide, m p 215°. It is reduced by zinc dust and acetic acid to physostigmine, and can be formed from this alkaloid by hydrogen peroxide. Geneserine is thus the amine oxide of physostigmine, with the additional oxygen atom probably attached to the basic nitrogen of the pyrrolidine ring In accordance with this it yields degradation products such as geneseroline, analogous to the corresponding products obtained from physostigmine. *Eseramine*, isolated by Ehrenberg (*l c*), is stated to have the formula $C_{16}H_{25}O_3N_4$ (which cannot be quite correct as to hydrogen). It remains in the ethereal solution after physostigmine has been extracted by dilute sulphuric acid (*see above*). It is sparingly soluble in ether, chloroform, or benzene, but readily so in hot alcohol, from which it crystallises in needles, m.p. 245°. The same alkaloid was isolated by Salway (*l c.*), who also obtained from the ethereal mother liquors left after the separation of eseramine, another alkaloid, *physovenine*, $C_{14}H_{18}O_3N_2$, which crystallised from light petroleum in small prisms, m.p. 123°. It is a weak base, very soluble in alcohol, benzene, or chloroform, moderately so in ether. It is evidently the acid carbonate of eseroline, HOOC O $C_{13}H_{17}N_2$. Whether it is formed from physostigmine by partial hydrolysis during the extraction, or whether it occurs as such in the beans, is uncertain. *Eseridine* was obtained by Bohringer und Sohne (Pharm. Post, 1888, **21**, 663), and subsequently by Eber (Pharm. Ztg 1892, **37**, 483) who assigned to it the formula $C_{15}H_{23}O_3N_3$ Its m p 132°, the fact that it is much less poisonous than physostigmine, and its conversion into the latter alkaloid by heating with dilute mineral acids suggest that eseridine is perhaps identical with geneserine.

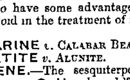
iso *Physostigmine*, $C_{15}H_{21}O_2N_3$, obtained by Ogui (Apoth.-Ztg. 1904, **19**, 891), is stated to be insoluble in ether and to form a crystalline sulphate, m p. 200°–202°. *Calabarine* of Harnack and Witkowski (Arch. exp. Path. Pharm. 1876, **5**, 401) has not been characterised chemically and was apparently a decomposition product of physostigmine, or derived from a mixed drug; it produced tetanic convulsions, like strychnine.

The *physiological* action of physostigmine depends on its inhibition of the hydrolysis of acetyl choline by choline-esterase (Loewi and Navratil, Pflüger's Archiv. 1926, **214**, 689; *see also* CHOLINE). Since acetyl choline is liberated in the nerve endings when parasympathetic nerves such as the vagus are stimulated, physostigmine brings about its stimulant effect on smooth muscle by preventing the hydrolysis of acetyl choline. Atropine paralyses the vagus and thus antagonises physostigmine. On the other hand, physostigmine resembles pilocarpine and muscarine in its physiological action, and produces, for example, powerful contractions of the intestine, on which its use as a veterinary purgative depends; it also stimulates salivary secretion. In human medicine it is principally used as a miotic, causing constriction of the pupil; atropine has the opposite effect (mydriasis). Geneserine has a weaker action than physostigmine on salivary secretion and no miotic action (Polonovski and Combemale, Compt. rend. Soc. Biol. 1923, **88**, 881). Rubreserine is inactive (Heubner, Arch. exp. Path. Pharm. 1905, **53**, 313); eseroline is likewise inactive; hence the physiological activity depends on esterification with carbamic acid, or with carbonic acid, for physovenine is also a very powerful miotic (Salway, *l c.*).

Synthetic Analogues of Physostigmine.—The above facts led Stedman (Biochem. J. 1926, **20**, 719; 1929, **23**, 17) to prepare a number of simpler urethanes by the action of various carbimides on dimethylamino phenols (Primary and secondary bases would react with the carbimides to form substituted ureas.) In this way a large number of bases have been prepared which, even at high dilutions, inhibit the action of liver esterase (Stedman and Stedman, Biochem J. 1931, **25**, 1147, 1932, **26**, 1214). For instance, the rate of hydrolysis of tributyrin was halved by a concentration of 1 500,000,000 of the hydrochloride of the *m* dimethylaminophenyl ester of methyl carbamic acid. Choline esterase is similarly inhibited and thus these urethanes act on the intestine and the pupil like physostigmine. One of them, *miotine*,



approaches closely to physostigmine in miotic activity (Stedman and Stedman, J C.S 1929, 609; White and Stedman, J. Pharm. exp. Ther. 1931, **41**, 259). A further series was examined by Aeschlimann and Reinert (*ibid.* 1931, **43**, 259) and the substance *prostigmine*,



was introduced as a substitute for physostigmine in post-operative intestinal stasis. Its actions on the pupil and on the intestine, as well as its toxicity, are very similar to those of physostigmine, but the dimethyl urethane grouping makes prostigmine rather more stable. The substance seems also to have some advantages over the natural alkaloid in the treatment of myasthenia gravis. G. B.

CALABARINE *v.* CALABAR BEAN.

CALAFATITE *v.* ALUNITE.

CALAMENE.—The sesquiterpene hydrocarbon, *calamene*, $C_{15}H_{24}$, b p 123°–126°/10 5 mm., d^{20}_{20} 0 9224, n^{20}_D 1·50572, $[\alpha]_D$ +5°, was first isolated by Kurbatov (Annalen, 1874, **173**,

4) from the rhizomes of *Acorus calamus* L. and has been studied more recently by Semmler and Spornitz (Ber. 1913, **46**, 3702) and by Ruzicka, Meyer, and Mingazzini (Helv. Chim. Acta, 1922, **5**, 358). Calamene contains two ethylenic linkages yielding on catalytic hydrogenation tetrahydrocalamene, b.p. 123°–125°/10 mm., d_{19}^{20} 0·8951, n_D^{20} 1·4848; it is a derivative of cadalene since it gives this hydrocarbon on dehydrogenation with sulphur. Its constitution is not known. J. L. S.

CALAMENOL. The alcohol *calamenol*, $C_{15}H_{24}O$, b.p. 150°–160°/17 mm., d^{20} 0·96115, n_D 1·5098, occurs in the oil from the rhizomes of *Acorus calamus* L. (Thoms and Beckström, Ber. 1901, **34**, 1021 ; 1902, **35**, 3187, 3195 ; Semmler and Spornitz, *ibid.* 1913, **46**, 3704 ; Ruzicka, Meyer, and Mingazzini, Helv. Chim. Acta, 1922, **5**, 358). It gives on dehydration a hydrocarbon, *calamenene*, $C_{15}H_{22}$, b.p. 136°–143°/15 mm., d_{19}^{20} 0·9324, n_D 1·5317 ; $[\alpha]_D$ +6°, and cadalene is formed on dehydrogenation with sulphur. J. L. S.

CALAMEON. The oxide *calameon*, $C_{15}H_{26}O_2$, m.p. 168°, $[\alpha]_D$ −8·94°, was isolated by Thoms and Beckström (Ber. 1901, **34**, 1021 ; 1902, **35**, 387) from the oil from the rhizomes of *Acorus calamus* L. In its properties it resembles somewhat 1:8-cineole and it yields on oxidation with potassium permanganate *calameonic acid*, $C_{15}H_{24}O_4,2H_2O$, m.p. 153°. J. L. S.

CALAMINE (*Galmei*, Ger.). Under this name two common zinc minerals—the carbonate, *smithsonite*, and the hydrous silicate, *hemimorphite*—are frequently much confused. The Latin form *lapis calaminaris* is supposed to be a corruption of the old name *cadmia* (*καδμία*) used for zinc ores in general. The minerals in question often so closely resemble one another in external appearance that it is only possible to distinguish them by chemical tests ; and it was not until 1803 that James Smithson definitely established the existence of the two distinct species. The name calamine was then applied by some authors to the carbonate (sparry calamine), and by other authors to the hydrous silicate (electric calamine). In 1832 F. S. Beudant proposed the name smithsonite for the carbonate, restricting the name calamine to the hydrous silicate ; but most unfortunately Brooke and Miller, in 1852, reversed these designations. Beudant has been followed by Dana and many other mineralogists, but in England the name calamine is unfortunately still much in use for the carbonate, and hemimorphite (G. A. Kenngott, 1853) for the hydrous silicate. The use of the latter name partly clears up the confusion, since it is descriptive of the very characteristic hemimorphic development of the crystals. The old name *zinc-spar* is also descriptive of the carbonate. L. J. S.

CALAMINE. A term applied to the basic zinc carbonate used in pharmacy.

CALAMUS *v.* ACORUS CALAMUS.

CALAMUS, ESSENTIAL OIL OF *v.* ACORUS CALAMUS.

CALAVERITE. A telluride of gold, $AuTe_2$, containing 40–43% of gold with 1–3% of silver. It was first found in Calaveras Co., California, and afterwards in considerable abundance in the Cripple Creek district in Colorado and at Kalgoorlie in Western Australia, where it is of importance as a telluride ore of gold. Sp.gr. 9·155–9·39. The small complex (monoclinic or triclinic) crystals from Colorado are tin-white in colour, tarnishing to bronze-yellow on exposure. The massive material from Kalgoorlie is pale bronze-yellow with bright metallic lustre; and with its sub-conchoidal fracture and absence of cleavage it much resembles iron-pyrites in appearance—in fact, before its value was recognised, the mineral had been thrown away on the waste heaps of the mines. L. J. S.

CALCIBRONAT. A preparation containing bromine and calcium gluconate (B.P.C. 1934).

CALCIDINE. Calcium iodide.

CALCIFEROL, or "**VITAMIN D_2**," is that form of the anti-rachitic vitamin which is produced by the irradiation of ergosterol. It was thought until lately that there was only one form of vitamin D, but recently it has been shown that there are several, and that the one present in fish liver oils is different from calciferol.

The identification of ergosterol as a pro-vitamin followed on a knowledge of the relation between ultra-violet rays and rickets. As long ago as 1890 Palm (Practitioner, **45**, 270) pointed out that the incidence of rickets was geographically associated with deficiency of sunlight. In 1919 Huldschinsky in Berlin (Deut. med. Woch. **45**, 712) treated rickets by means of actino-therapy. Animal experiments soon revealed the fact that rickets could be prevented either by irradiation of the animal (Hess, Unger, and Pappenheim, J. Biol. Chem. 1922, **50**, 77) or of the food it ate (Hess and Weinstock, J. Biol. Chem., 1924, **62**, 301 ; Steenbock, Science, 1924, **60**, 224). Various food constituents were tested in turn by irradiation, and it then became apparent that the precursor of vitamin D was present in the cholesterol fraction. For a time cholesterol was itself regarded as the pro-vitamin, but it was later shown that with re-purification cholesterol lost its power to be activated, so that the pro-vitamin was to be regarded as an impurity in ordinary specimens of cholesterol. Various likely sterols were thereupon irradiated and tested for anti-rachitic activity, and in 1927 ergosterol ($C_{28}H_{44}O$) was identified as the parent substance (Rosenheim and Webster, Biochem. J. 1927, **21**, 127, 389 ; Lancet, 1927, **1**, 306 ; **2**, 622 ; Nature, 1927, **120**, 440 ; Windaus and Hess, Proc. Soc. exp. Biol. N.Y. 1926–1927, **24**, 171, 369, 461 ; Nach. Ges Wiss. Göttingen, Math.-Physik, 1927, **2**, 175), or, as we should now say, one of the several pro-vitamins. Ergosterol is a principal representative of the sterol group of compounds found in numerous fungi, moulds, yeasts, etc., and was first separated from ergot by Tanret in 1890. The transformation which takes place during the ultra-violet irradiation of ergosterol is a photochemical reaction, during which

a mixture of various isomers are formed, only one of which is the actual vitamin. Windaus, Lüttringhaus, and Busse (Nach. Ges. Wiss. Göttingen, Math.-Physik. 1932, 3, 150) summarised the chain of reactions as follows:

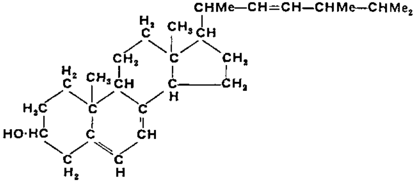
1. *Effect of Irradiation.*—

ergosterol → lumisterol → calciferol → suprasterol I
calciferol → suprasterol II
calciferol → substance absorbing at 248 $m\mu$
lumisterol → tachysterol

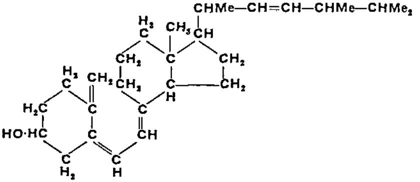
2. *Effect of Heat.*—

calciferol → pyrocalciferol+*iso* pyrocalciferol
tachysterol → pyrotachysterol

A later view is that tachysterol is an intermediate product between lumisterol and calciferol, but there is no doubt that these various transformation products are formed concurrently in somewhat varying amounts depending on the conditions of irradiation (*see* Setz, Z physiol. Chem. 1933, 215, 183). The separation of the crystalline vitamin from the irradiation mixture was accomplished in 1931–1932 at the two laboratories where ergosterol had first been identified as a pro vitamin (Askew, Bourdillon, Bruce, Callow, Philpot, and Webster, Proc. Roy. Soc. 1932, 109, B, 1488; Windaus, Linsert, Luttringhaus, and Weidlich, Annalen, 1932, 492, 226). The London workers relied on the formation of the 3:5-dinitrobenzoate ester for the purification, and those at Gottingen made use of fractional crystallisation after treatment with maleic and citraconic anhydride. Bourdillon and co-workers proposed the name "calciferol" for the crystalline vitamin so prepared, and Windaus and his collaborators "vitamin D_2." (The name "vitamin D_1" was applied to a molecular compound of calciferol with lumisterol, which had been previously isolated, and a similar molecular compound of vitamin D and pyrocalciferol was also at first called "calciferol" by Bourdillon *et al.* in the belief that it was the pure vitamin itself.) The conversion of ergosterol into calciferol involves scission of ring II and is represented in the scheme given below (*see* Windaus and Thiele, Annalen, 1935, 521, 160; Heilbron, Jones, Samant, and Spring, J.C S 1936, 905).



Ergosterol.



Calciferol.

This same transformation of ergosterol into calciferol takes place not only under the influence of ultra-violet rays but with X-rays, cathode rays, or a glow discharge.

Calciferol has about 400,000 times the antirachitic potency of cod-liver oil and it has been calculated that 1 oz. of it would be enough to protect 3,000 children for 1 year. The rat dose is 1/100,000 mg. per day. Calciferol is readily soluble in the usual fat solvents. It gives colour reactions with a number of reagents, and various ester like derivatives have been prepared from it. It shows selective absorption at 265 $m\mu$.

Other substances with vitamin D activity, all of which are closely related to calciferol in chemical structure, are the following: (1)

irradiated 7-dehydrocholesterol (or "vitamin D_3"), intensely active, with a potency (for rats) about one-half of that of calciferol itself (Windaus, Lettré, and Schenck, Annalen, 1935, **520**, 98; Windaus, Schenck, and *von* Werder, Z. physiol. Chem. 1936, **241**, 100); (2) irradiated 22:23-dihydroergosterol (Windaus and Langer, Annalen, 1933, **508**, 105; McDonald, J. Biol. Chem. 1936, **114**, proc. lxv); (3) irradiated 7-dehydrositosterol (Wunderlich, Z. physiol. Chem. 1936, **241**, 116), whilst (4) irradiated 7-dehydrostigmasterol (Linsert, Z. physiol. Chem. 1936, **241**, 125) is practically inactive. Less well defined are (5) irradiated heated-cholesterol, moderately active (Koch, Koch, and Ragins, J. Biol. Chem. 1929–1930, **84**, 141); (6) cholesterol activated *without light* by means of fullers' earth=cholesterilene sulphonic acid, or its Ca or Ba salt (Bills, J. Biol. Chem. 1926, **67**, 753). "Natural" vitamin D from tunny liver oil is different from calciferol (Ender, Z. Vitaminforsch. 1933, **2**, 241; 1934, **3**, 161) and is identical with 7-dehydrocholesterol ("vitamin D_3") (Brockmann, Z. physiol. Chem. 1936, **241**, 104; 1937, **245**, 96; Haslewood and Drummond, Chem. Ind. 1936, **55**, 598).

Evidence is increasing that the *natural* vitamin D and pro-vitamin D present in vegetable sources (including flowering plants and cryptogams) is not identical with that found normally in animal sources. Probably the natural vitamin found in plant tissues which have been exposed to sunlight is identical with calciferol, or at any rate has calciferol as a main component (*see* Bethke, Record, and Wilder, J. Biol. Chem. 1935, **112**, 231). Bills (Physiol. Reviews, 1935, **15**, 1; Cold Spring Habor Symposium on Quantitative Biology, 1935, **3**, 328) believes that there may also be several natural forms of the vitamin present in different fish-liver oils.

Vitamin D activity seems to depend, in all the substances mentioned above, on the presence of the three ring structure with the three conjugated double bonds of calciferol, the structure of the side chain being apparently relatively unimportant.

The differentiation of calciferol from these other forms of vitamin D had its origin in the observation that calciferol was less effective as an antirachitic for chickens than was the same number of "rat units of vitamin D" given as cod-liver oil (Carrick, quoted by Bills, Physiol. Reviews, 1935, **15**, 1; Massengale and Nussmeier, J. Biol. Chem. 1930, **87**, 423). L. J. H.

CALCINOL. Calcium iodate.

CALCIOCORAMINE. Double salt of pyridine-β-carboxyldiethylamide and calcium thiocyanate. Prescribed for bronchitis (Ciba, London), B.P.C. 1934.

CALCITE or CALC-SPAR. One of the dimorphous crystallised forms of calcium carbonate ($CaCO_3$). This rhombohedral form is less dense (sp.gr. 2·72) and less hard (H. 3) than the orthorhombic form aragonite (*q.v.*). It is also the more stable form: when aragonite is heated to low redness it passes into calcite, and paramorphs of calcite after aragonite are of frequent occurrence in nature. From an aqueous solution containing carbon dioxide, calcium carbonate crystallises as calcite at temperatures of 0°–18°, and as a mixture of calcite and aragonite at higher temperatures: the presence of various salts in the solution also favours the formation of aragonite. (For a summary of the literature on the crystallisation of calcium carbonate, *see* F. Vetter, Z. Kryst. Min. 1910, **48**, 45.) Calcite may be readily distinguished from aragonite by the possession of three perfect cleavages parallel to the faces of the primary rhombohedron, the angles between which are 74° 55′ and 105° 5′ (the plane angles on the rhomb-shaped faces are 78° and 102°). The mineral is readily scratched with a knife, and it effervesces briskly in contact with cold dilute acids.

With the exception of quartz, calcite is the commonest of minerals. It frequently occurs well crystallised and in a great variety of forms, the various forms of its crystals suggesting the trivial names "dog-tooth-spar," "nail-head-spar," "paper-spar," "cannon-spar," etc. As the essential constituent of the rocks limestone, marble and chalk, it is of abundant occurrence. In these forms it finds extensive applications as building and ornamental stones, and in the manufacture of lime, mortar and cement.

The clear, transparent variety, known as Iceland-spar or doubly-refracting spar, is used in the construction of Nicol prisms for optical polarising apparatus. Material suitable for this purpose is obtained almost exclusively from a quarry in basalt on the Reydar-fjördhr on the east coast of Iceland, but the supply is limited and variable. Clear material suitable for optical work has also been found between Greycliff and Bigtimber in Montana, where it occurs in vertical veins in gneiss; and in the Kenhardt district, Cape Province, South Africa. L. J. S.

CALCIUM. Symbol, Ca; at. no. 20; isotopes 40, 42, 43, 44; at. wt. 40·085.

Calcium is an original constituent of the "sial," the outer crust of the earth, in which it occurs mainly as oxide in combination with silica. The amount in the igneous rocks varies from slightly over ½% in the extreme acid granites to 12% in the ultra-basic rocks. The amount of solids in the original ocean must have been extremely small at the time they were deposited from the vapour and gases forming the atmosphere; consequently, the calcareous sedimentary rocks produced either by chemical precipitation or by marine organisms must have come largely from the weathering of the original solidified crystalline crust. The second source of calcium as well as of many other elements is from hot springs, but the composition of these varies considerably; in some the amount of calcium is insignificant, whereas in the hot springs of Palestine calcium chloride is one of the principal constituents (*see* BROMINE, p. 108).

The main mass of calcium now exists as carbonate deposited from the ocean largely by marine organisms. In the long history of the earth's crust the more calcareous marine sediments have been consolidated to soft and hard limestones or altered by metamorphism to marble. Replacement of the calcium by magnesium produces magnesium limestone or

dolomite, $CaCO_3,MgCO_3$. Calcium also occurs abundantly as the sulphate or gypsum, $CaSO_4,2H_2O$, deposits of which have mainly resulted from desiccation of detached bodies of sea water. Calcium phosphate (apatite) is a common constituent of the primary rocks and is the principal mineral ingredient of the vertebrate skeletons which, with coprolites, form the main part of bedded phosphate deposits (*v* ASH)

Preparation of the Metal.—Calcium was obtained as an impure metallic powder by Davy in 1808, by the electrolysis of the chloride, using mercury as negative electrode, and afterwards heating the amalgam thus formed until the mercury volatilised

Moissan obtained calcium by heating anhydrous calcium iodide (600 g) with metallic sodium (240 g) at a dull red heat. After allowing the melt to cool the metallic portion was cut up and digested with alcohol which dissolved the excess of sodium leaving the calcium in brilliant white crystals 98 9 to 99 2% pure.

Ruff and Plato succeeded in obtaining the metal in relatively large quantities by the electrolysis of fused calcium chloride by keeping the temperature of the cathode above the melting point of calcium (U.S.P. 806006). Borchers and Stockhem, by electrolysing fused anhydrous calcium salts, keeping the temperature of the cathode below the melting-point of calcium, obtained the metal in a spongy state (U.S P. 808066) By using a vertical cathode, which only just touches the surface of the fused calcium salt, the metal is deposited on this surface and by mechanically raising the cathode an irregularly shaped rod of calcium, resembling a cabbage stalk, is formed, which itself forms the cathode (B.P. 20655, *cf* Johnson, Ind Eng Chem. 1910, 2, 466). The electrolyte, consisting of a fused mixture of 10 parts of $CaCl_2$ with 17 parts of CaF_2, is contained in a cylindrical vessel of Acheson graphite The containing vessel forms the anode, whilst the cathode is an iron ribbon which can be run up from below. The best deposits were obtained with a current density of 10 amperes per sq cm. If the cathode current density is too high the metal does not adhere, whilst if the anode density is too low the electrolyte is not all melted, and for proper control the anode and cathode surfaces should be defined for the conditions in use Moldenhauer and Andersen (Z. Elektrochem 1913, 19, 444) used a mixture of 85% $CaCl_2$ with 15% KCl and a current density of 60–110 amperes per sq cm. Rods 9–18 mm diameter were obtained, containing Ca 96 09–98 18, K 0 0–0 14, Fe 0·3–0 4, Si 0 40–0 70%. The current yield varied from 56 to over 90%.

Commercial calcium is usually coated with $CaCl_2$, which can be partly removed by absolute alcohol, and the remainder by re melting in an iron bomb. In this way a metal containing 99 44% Ca and 0 25 $Al_2O_3+SiO_2$ is obtained

Metallic calcium is gradually acquiring new commercial application. Among the more important are the debismuthising of lead (the Betterton process); the hardening of lead for various purposes, particularly bearing metal and cable coverings; as a deoxidant for copper and its alloys and for cast iron and steel; as a constituent of aluminium alloys; as a reducing agent for oxides of beryllium, chromium, thorium and uranium; as a desulphurising agent in petroleum refining; and as an adsorbent of residual gases in vacuum tubes (Mantell and Hardy, Trans. Electrochem. Soc. 1934, 66, 187).

The metal has m p. 851°±1° (von Antropoff and Falk, Z. anorg. Chem. 1930, 187, 405; Hoffman and Schulze, Physikal. Z. 1935, 36, 453), b p. 1712°±5° (Hartmann and Schneider, Z. anorg. Chem. 1929, 180, 275). Its electric conductivity is 16, that of silver being 100. It may be turned into cylinders having a brilliant lustre tarnishing in air, or drawn into wire of 0 5 mm. diameter.

Calcium is a silver-white metal, less malleable than sodium or potassium; it scratches lead but not calcite. It can be cut with a knife or broken with a blow, and the fracture is crystalline; the crystals are of tabular habit and belong to the rhombohedral system.

P. Bastien (Compt. rend. 1934, 199, 577) gives the coefficient of cubic expansion of Ca (99 3%), prepared by sublimation and subsequent fusion in argon, as $25\ 2\times10^{-6}$ over the range 20°–100°, and $d^{20}=1{\cdot}542\pm0\ 0005$.

Zalesinski and Zulinski (Bull. Acad. Polanaise, 1928, (A), 479) obtained the following figures for the sp ht. of calcium between 20°–304°, 0 1610; 20°–504°, 0 1764; 22°–520°, 0 1768, 20°–697°, 0 1887; 21°–755°, 0 1927, 22°–785°, 0 1901; 22°–785°, 0 1724; 22°–802°, 0 1724; 810°–930° (liquid), 0 2670 The lower values were obtained by first heating to 800° and are due to the existence of an allotropic modification formed at the higher temperatures.

Calcium inflames when heated in oxygen to 300°, and the heat is so great that the lime formed is both fused and partly volatilised. Fluorine gas violently attacks calcium at the ordinary temperature. Chlorine, bromine and iodine have no action until heated to 400° or above.

Gently heated in air, it burns with incandescence, or heated in a current of air at a dull red heat it leaves a spongy mass which decomposes water, producing ammonia and calcium hydroxide. Calcium, therefore, fixes both nitrogen and oxygen.

Metallic calcium exists in an active and an inactive form (α- and β-) as regards its power of adsorbing gases (Franck and Bodea, Z angew Chem. 1931, 44, 382) Active calcium commences to adsorb nitrogen at 300°, and has a maximum action at 440°. As the temperature increases the rate of combination slowly decreases, until at 800° it has ceased. The velocity of adsorption is dependent on the presence of a layer of nitride. The inactive form commences to combine with nitrogen at 800°. The active variety is prepared by slowly cooling molten calcium. This variety produces a black nitride (Sieverts, Z. Elektrochem 1916, 22, 15).

H. Hartmann and H. J. Frohlich (Z. anorg. Chem. 1934, 218, 190) find that the combination of N_2 with pure Ca, free from alkali and N, ceases as soon as a thin layer of Ca_3N_2 has been formed on the surface. With Ca activated

by $<1\%$ Na, the velocity of N adsorption depends on temperature. Two modifications of Ca_3N_2 have been obtained, a pseudo-hexagonal form (I) at 300°, *a* 3·553, *c* 4·11 Å., *d* calc. 2·72, and a cubic form (II) at 800°, *a* 11·38 Å., *d* calc. 2·66. (II) is obtained when (I) is heated at 500° (*cf.* Franck *et al.*, 1933, A. 666).

Rinck (Compt. rend. 1931, **192**, 421, 1378) states that using calcium distilled in vacuum (m.p. 848°) the data obtained in an atmosphere of argon afford no evidence of compound formation. α-Calcium is stable below and β-calcium stable above 450°.

Calcium decomposes water at the ordinary temperature with the liberation of hydrogen; the action is slow, owing to the formation of a crust of calcium hydroxide; the addition of sugar hastens the action. Fuming nitric acid attacks the metal if free from lime only slowly; the action is hastened by dilution. Fuming sulphuric acid is immediately reduced in the cold to sulphur and sulphur dioxide. Hydrochloric and acetic acids attack calcium violently, with the liberation of hydrogen. At a red heat, calcium reduces the fluorides and chlorides of potassium and sodium, setting free the alkali metals; under the same conditions, the iodides are not attacked.

Calcium Mercurides.—Eilert (Z. anorg. Chem. 1926, **151**, 96) states that calcium has little action on mercury at the ordinary temperature, but when heated at 340° brisk reaction occurs in which the mercury takes up 3% of calcium. The calcium used was 99·2% pure, practically all the residue being enclosed CaO. Thermal analyses with photo-micrographs show that crystals of $CaHg_3$ are precipitated from calcium amalgam containing more than 2·15% by weight of calcium. At 26·5° this compound reacts with a melt containing 2·15% calcium to form crystals of $CaHg_5$. The reaction proceeds to completion. The existence of the compound $CaHg_5$ has been confirmed by analysis of an individual crystal. Neuhausen (J. Amer. Chem. Soc. 1922, **44**, 1445) employed a 25-cm. dish containing a thin layer of Hg filled with 1·75 *N*-solution of $CaCl_2$, an anode of platinum foil, 2×4 cm., was placed parallel at 4 cm. distance from the mercury. A current 3·5 amperes at 4·6 volts was passed for 30 minutes, after which hydrogen was evolved. The amalgam was washed by pouring into distilled water and contained 0·069–0·075% calcium.

Alloys.—*Sodium.*—Calcium, although soluble in molten sodium, from which it separates in the crystalline state on solidification of the solvent, is not notably soluble in potassium.

In the system $CaCl_2+2Na \rightleftharpoons Ca+2NaCl$ at 600°–800° the metal phase has a constant composition, *e.g.* at 0·95 atom % Ca and 99·05 atom % Na when the salt phase contains 16–98·5 molecular percentage composition of calcium chloride. The total solubility of sodium and calcium at constant temperature in a fused mixture of sodium and calcium chlorides increases in an approximate manner with the calcium chloride concentration, and rapidly with rise of temperature (Lorenz and Winzer, Z. anorg. Chem. 1929, **181**, 193).

The liquidus of the Ca–Na system is horizontal at 710° from 7 to 86% Ca, Ca being soluble in Na to the extent of 7% and Na in Ca to 15%. Complete miscibility occurs at 1,185° (Rinck, *l.c.*).

Aluminium.—Matsuyama (Sci. Rep. Tôhoku, 1928, **17**, 783) finds that the liquidus of the Al–Ca system consists of four branches corresponding with separation of a solid solution, $CaAl_3$, $CaAl_2$, and Ca respectively. Aluminium dissolves 0·3% calcium at ordinary temperature and 0·6% at 616°. Alloys containing 0·6–33·03% calcium are eutectiferous, the eutectic containing 7·55% calcium and melting at 616°. Alloys containing 13·9–42·5% calcium undergo a peritectic reaction on cooling below 700° forming $CaAl_3$. The liquidus has a maximum of 1,079° at 42·5% calcium corresponding with $CaAl_2$. Alloys containing more than 42·5% calcium are eutectiferous, the eutectic containing 73% calcium and melting at 545°. Quantities of calcium up to 5% cause brittleness and a decrease in the tensile strength of aluminium.

Magnesium.—Calcium furnishes an alloy with magnesium which decomposes cold water. The freezing-point curve has a simple form, the single compound Ca_3Mg_4 being indicated by a maximum at 715°, whilst there are eutectic points at 514° and 446° and 18·7 and 78·7% of Ca respectively. The compound $CaMg_2$ is brittle, silvery in appearance, stable in air, and is only slowly acted upon by water.

Lead.—Lead and calcium react together violently in the molten state; the freezing-point curve has maxima at 649° and 1,105°, corresponding with the compounds $CaPb_3$ and Ca_2Pb respectively. Another compound, CaPb, is formed at 950°. All these alloys fall to a black powder in air.

Copper.—Copper and calcium form a single compound, $CaCu_4$, melting at 933°, unstable in air.

Silver.—Thermal measurements have suggested the existence of a number of silver-calcium compounds. C. Degard (Z. Krist. 1935, **90**, 399) has shown that when the alloys are melted in vacuum and examined by X-rays, the only compounds indicated are AgCa (face-centred cubic, *a* 9·07 Å.) and Ag_3Ca (tetragonal, *c/a* 0·88). There is no evidence for $AgCa_2$, Ag_4Ca, and Ag_2Ca.

Zinc, Nickel and Tin.—With zinc and nickel calcium forms brittle alloys. Tin, heated just above its point of fusion, combines with calcium with incandescence forming a white crystalline alloy containing 3·82% calcium.

Calcium Hydride, CaH_2.—Calcium does not unite with hydrogen at the ordinary temperatures. The hydride is obtained as a fused white solid, sp.gr. 1·7, when calcium cut into small pieces contained in several nickel boats is placed in a glass tube sealed at one end and hydrogen is fed in at a pressure of 4 to 5 cm. mercury, the tube being heated to redness, and the temperature kept sufficiently low to prevent union between the calcium and the nickel.

The adsorption of hydrogen by calcium and its alloys has been determined by Kassner and Stempel (Z. anorg. Chem. 1929, **181**, 83). At 250° calcium filings quickly adsorb hydrogen in

amounts corresponding with the formula CaH_2. At higher temperatures adsorption is slower, probably owing to sintering of the dihydride formed, and at 500° conversion into the *hydride is complete in 2–3 hours. At 800°* the velocity of adsorption becomes large again. The dissociation pressures of calcium hydride as determined by Kraus and Hurd (J. Amer. Chem. Soc. 1923, **45**, 2564) are at 985·6°, 4·82; 769·2°, 0·93; 734°, 0·42 cm. mercury.

Calcium hydride may be heated to redness in air without change. Its characteristic reaction is the decomposition of water in the cold with the liberation of hydrogen. It shows a marked dissociation from 600°, reaching 1 atmosphere pressure *below 800°. This cannot be a true* dissociation pressure, as the hydride is readily formed by heating calcium in hydrogen at 830°. A second hydride may also exist.

$$Ca+H \rightarrow CaH+23{,}100 \text{ g.-cal.};$$
$$CaH+H \rightarrow CaH_2+22{,}000 \text{ g. cal.}$$

(Bronsted, (Z. Elektrochem. 1914, **20**, 81) Moldenhauer and Roll-Hansen (Z. anorg. Chem. 1913, **82**, 130) calculate the heat of formation of calcium hydride from solution in hydrochloric acid: for CaH from liquid calcium and hydrogen about 21,000 g cal., and for CaH_2 from CaH and hydrogen 21,000 g.-cal. Guntz and Bassett (Compt. rend. 1905, **140**, 863) found 46,200 g.-cal. from solid calcium. The vapour-curve *between 755° and 920° can be represented by* the equation:

$$\log p = -3\,475 + 0\,005322T$$

The vapour pressure is considerably higher than that measured by previous investigators, corresponding with the equation:

$$2CaH_2 \rightleftharpoons 2CaH+H_2,$$

and not with the equation $2CaH \rightleftharpoons 2Ca+H_2$. The heat of reaction calculated according to van *'t Hoff's equation has the value 24·8 kg.-cal.* rising to 31·5 kg. cal. at 755° and 920° respectively, whilst the Nernst formula gives the value 22·6 kg.-cal. Calcium hydride in the form of water clear, hexagonal prisms with superimposed rhombohedra was prepared (Kassner and Stempel, Z. anorg. Chem. 1929, **181**, 83).

H. Flood (Kong. Norske Vid. Selsk. For. 1934, **7**, 66–69; 1935, A 1469) has shown that the primary reaction between CaH_2 and H_2O is to give CaO, but at low temp. <2 mols. of H_2 per mol. of CaH_2 are evolved, owing to the low v.p. of $Ca(OH)_2$. Above 350° reaction proceeds directly to CaO, and the drying effect of CaH_2 is most intensive.

A mixture of $BaSO_4$ and CaH_2 ignited by a *fuse similar to that used with thermite reacts* vigorously according to the equation:

$$BaSO_4+4CaH_2 = BaS+4CaO+4H_2,$$

(Ebler and Herrdegen, Ber. 1913, **46**, 2264).

Calcium Oxide. *Lime*, CaO.—Anhydrous calcium oxide (quicklime) is obtained by heating to redness any salt of calcium containing a volatile acid, such as the carbonate and nitrate. Calcium carbonate may be fused without decomposition when heated in a closed vessel, but when raised to a red heat under ordinary pressure it becomes converted into lime:

$$CaCO_3 = CaO+CO_2.$$

To obtain pure lime, Iceland spar or other forms of calcite, or the finest marble, may be employed, the ignition being performed in a crucible with perforated base so as to permit of the entrance of furnace gases, which carry away the carbon dioxide as fast as it is formed; *otherwise, the decomposition is incomplete*, the carbonate undergoing no change in an atmosphere of carbon dioxide. The tension of dissociation of $CaCO_3$ is 27 mm. at 547° and 753 mm. at 812°.

Measurements of the thermal dissociation of calcium carbonate by J. C. Southard and P. H. Royster (J. Physical Chem. 1936, **40**, 435), made with the use of a furnace in which a temperature of 900° could be maintained constant within 0·04° for over 30 hours, lead to pressures given by $\log_{10} p$ cm. $= -9140/T + 0\,382 \log_{10} T - 0\,668 \times 10^{-3}T + 9\,3171$. The temperature corresponding with 1 atmosphere is 894·4°. In practice, the temperature for burning lime is about 1,000°. The raw material may be nearly pure calcium carbonate, such as marble or chalk, or may contain so much clayey matter that the product is a cement of the Portland class rather than a lime. On this fact the choice of the mode of burning in part depends, because if the lime is needed to be pure it must be burnt out of contact with solid fuel, whereas if it is a cement rather than a lime, the addition of siliceous matter from the ash of the fuel may be actually an advantage. The chief uses of lime are for *building, in agriculture, and for chemical* manufacture. For the first purpose an impure limestone, burnt in contact with solid fuel, is to be preferred, whereas the purest obtainable limestone, heated out of contact with fuel, yields the best material for chemical use. In practice these principles are not always observed, partly from want of realisation of their validity and partly because it is sometimes economical to sacrifice the purity of the product rather than incur the expense in capital and fuel of kilns designed to burn limestone *out of contact*

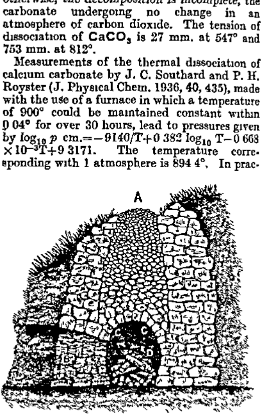


FIG. 1.

with solid fuel. The knowledge of these principles, however, is of value in deciding on the type of kiln to be adopted in any given case.

The simplest form of kiln is the flare kiln, shown in Fig. 1. The fuel (wood or peat) is burnt under an arch made of the material to be calcined, thus the lime produced is uncontaminated with ash. So crude a device is, of course, not economical of fuel, but its simplicity and cheapness, and the fact that it can produce excellent lime, cause it to be still used to a considerable extent, particularly where brushwood and limestone occur together. The greater part of the lime used in the Near East is produced in this manner.

Another simple form is the common running kiln shown in Fig. 2. The limestone or chalk

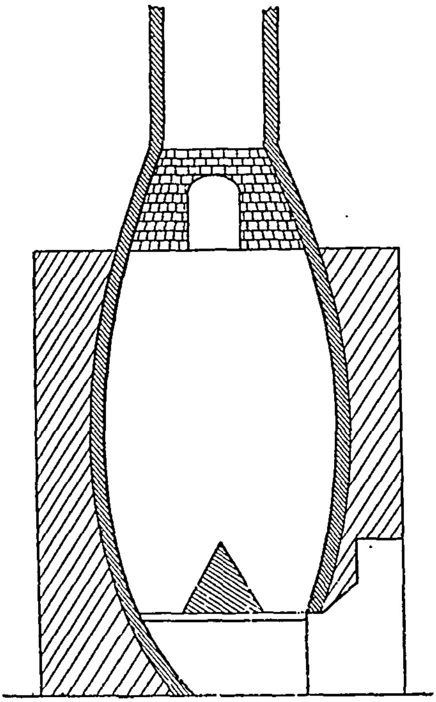


FIG. 2.

is loaded into the kiln with alternate layers of small coal or coke, and the product is from time to time drawn from an eye at the bottom of the kiln, fresh layers of raw material and fuel being added through the charging hole at the top of the kiln. Lime made in kilns of this class, of course, contains the whole ash of the fuel.

W. Woodhouse (J.S.C.I. 1932, 51, 115) states that the continuous vertical type of kiln produces the greater part of the lime used in England. The charge consists of alternate layers of limestone and coal, the lime being drawn at the bottom as the burning proceeds. The lime, however, is mixed with fuel ash. This type of furnace is most satisfactory when fired from exterior furnaces by coal or gas in which secondary air supplies assist in regulating the temperature.

The shaft differs considerably in details of shape and size. Most of them, however, are of cylindrical shape bulging from the top towards the hot zone and narrowing at the base.

In the Buxton area this type is still much in use. The height is generally about 50 ft., and where built into the side of the hill they are lined with one cover of fire brick. The limestone which has thin beds and pockets of clay is first disintegrated by a main blast tunnel and the blocks broken by small charges of black powder and then by hand, the small blocks being carefully sorted.

In America as in England the common kiln is the vertical type, known there as the keystone kiln. Its construction is shown in Fig. 3.

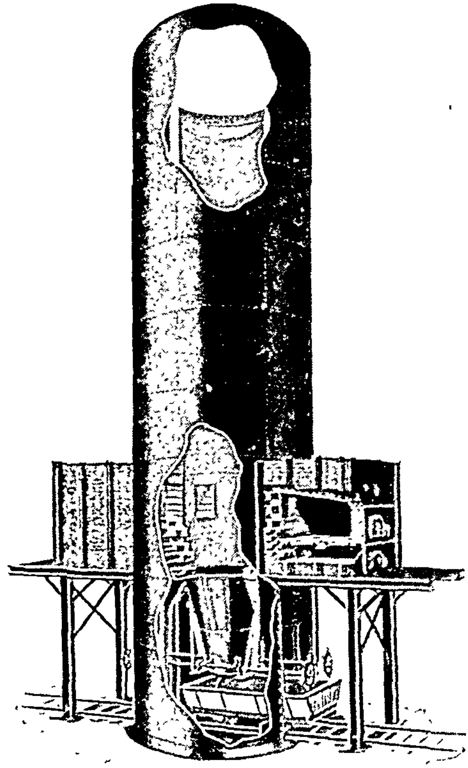


FIG. 3.

(Reprinted by permission from "Cements, Limes and Plasters," by Eckel, published by John Wiley and Sons, Inc.)

It consists of a heavy steel shell lined with fire brick. Eckel gives the following dimensions:

Outside diameter of shell . .	10 ft.	$11\frac{1}{2}$ ft.	12 ft.
Inside diameter of lining . .	5 ft.	6 ft.	$6\frac{1}{2}$ ft.
Total height. .	38 ft.	43 ft.	48 ft.
Output per day .	7–8 tons	8-10 tons	10–12 tons

Two furnaces are carried on steel platforms on opposite sides of the kiln in which coal is burnt. Below the level of the furnaces is a cooling cone made of steel plates from which the lime is withdrawn through draw gates.

Most of the recent modifications are variations of this type; patents and secret improvements in

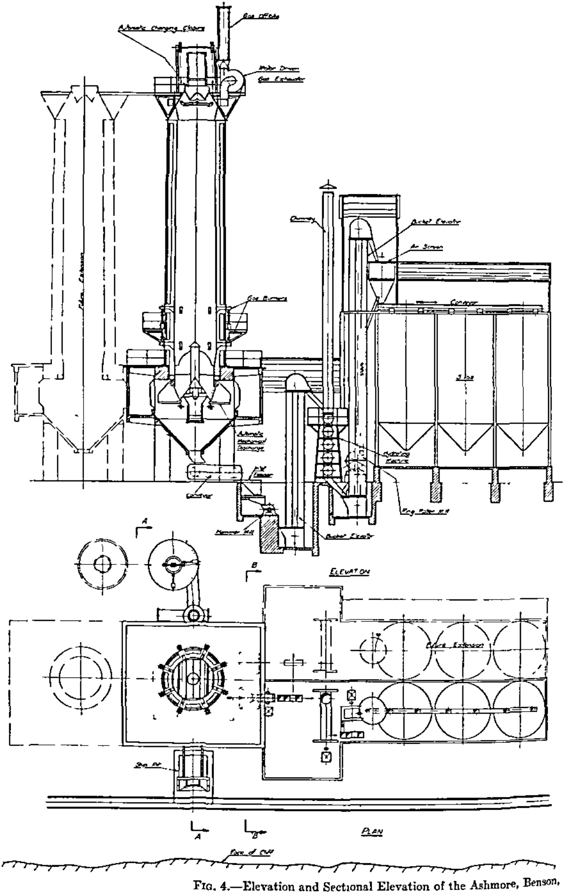
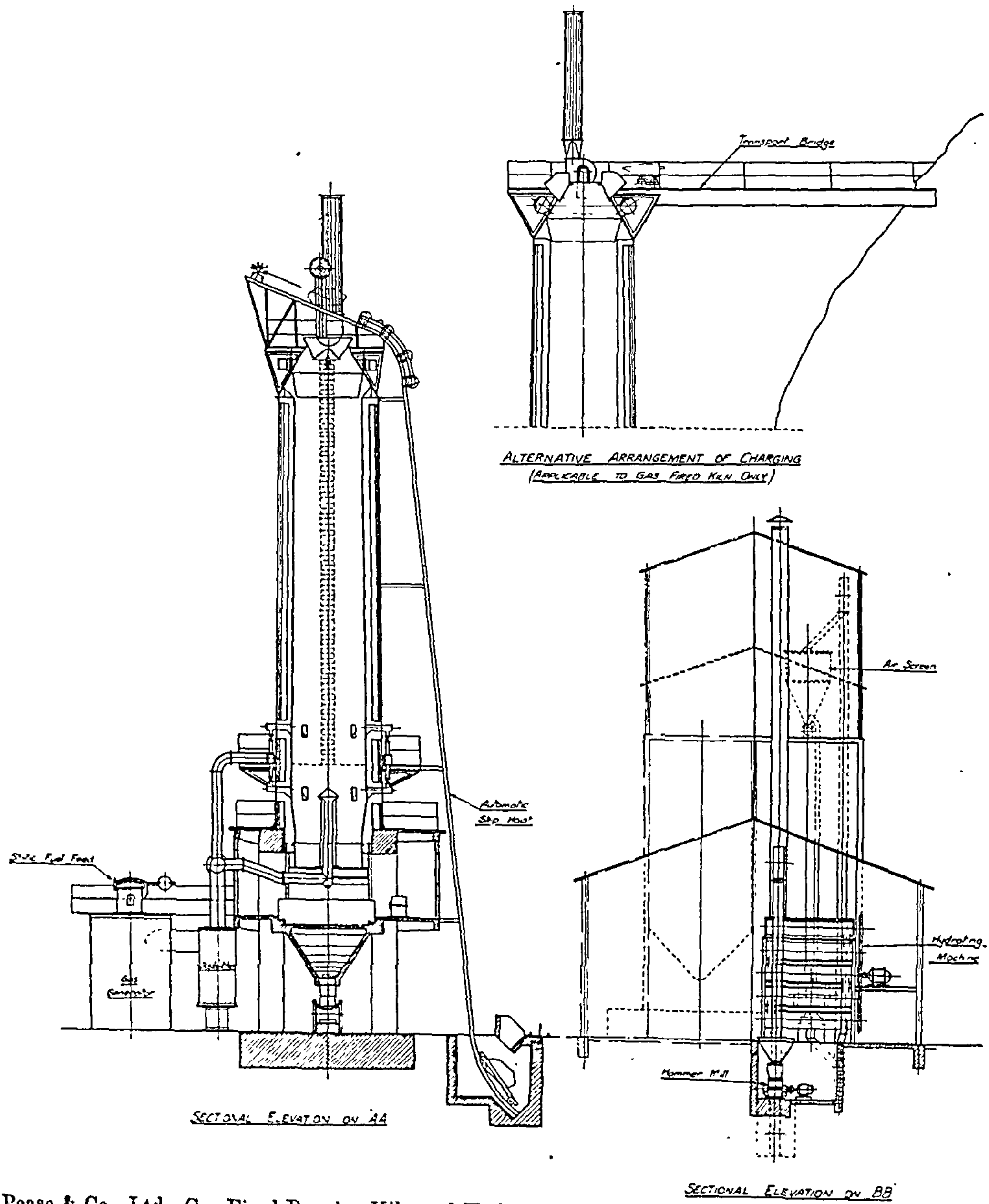


FIG. 4.—Elevation and Sectional Elevation of the Ashmore, Benson,

England are all connected with this type of furnace to produce a pure lime. The main difficulty in working is to maintain uniform heating of the limestone.

In Germany the tendency is towards the use of gas-fired shafts, particularly in areas where brown coal occurs, the gas being manufactured by means of a gas producer. These furnaces are usually about 14·5 m. high, width 1·6 m. at the top and 1·85 m. at the bottom of the inside of the shaft. Generally they are built in pairs, as is common in most of the shaft furnaces in England, but in some cases, as illustrated in "Das Kalkbrennen" by B. Block, 1924, six furnaces are built into an angular structure in which the interior of the shaft becomes six-sided, giving a distance from centre to centre shaft of the ring of 8·65 m. In England the steel shaft kiln fired by producer gas is gradually replacing the older mixed fuel type.

The modern type of kiln made by Messrs. Ashmore, Benson, Pease & Co., Ltd., at their Parkfield Works, Stockton-on-Tees, and illustrated in Fig. 4, is supplied complete with gas producer and hydrating equipment. The kiln is approximately 70 ft. in height from the charging bell to the automatic mechanical discharge; 9 ft. diameter at the top tapering to $9\frac{1}{2}$ ft. diameter at the level of the gas burners.



Pease & Co., Ltd., Gas-Fired Burning Kiln and Hydrating Plant.

A kiln of the foregoing dimensions and type will produce 40 tons of burnt lime per day of 24 hours

The kiln consists of a steel cylindrical shell of riveted or welded construction with an inner lining of fire brick and a layer of heat insulating material between the steel shell and the fire-brick lining.

The firing arrangements for the kiln comprise two circular mains one above the other, each main being fitted with eight separate burners situated at a suitable height above the discharge A specially constructed central burner injects a flame into the centre of the kiln on a level with the lower set of burners, thus ensuring a uniform temperature in the heat zone with complete burning of the lime

The kiln is charged from ground level by means of an automatic skip hoist, or arrangements can be made for direct charging by means of bogies in places where the contour of the surrounding site permits

The kilns are provided with automatic labour saving devices for the production of hydrate of lime.

Lime can be burnt in a rotary kiln similar to those used for cement but worked at a lower temperature

The Hoffmann kiln is used in places where labour is sufficiently cheap to allow of loading and unloading by hand being performed at a low cost, as in the Buxton area, and it has the advantage of being economical of fuel It is largely used in America The limestone must be crushed and graded to ½–1½ in size The burning chamber consists of an endless tunnel, divided into compartments of approximately equal size by means of combustible dampers. Each chamber is provided with an opening in the outside wall for charging and discharging, and with an opening into the main flue connecting with the chimney. The fuel of breeze and coal is introduced through holes in the arched roof. The kiln is worked on a progressive scheme, fuel being charged into the hottest chamber, and air being allowed to enter here so as to complete the calcination, while the gases are allowed to escape through dampers in the last chamber. The daily production of these furnaces is very large.

The divisions are made with brown paper which burns as the heat extends and allows the heated gases to attack the limestone in the next chamber. One of these furnaces has been in use at the Buxton Lime Co. Works for fifty years.

A. B Searle, "Limestone and its Products," Benn, 1935, states that the total length of the tunnel should not be less than 168 ft, and 240 ft is preferable. The latter will allow of 20 chambers (charging sections) each 12 ft. in length. In such a kiln running normally:

1 chamber will be empty.
1 chamber will be filling.
7 chambers will be preheating by hot gases from the fuel.
4 chambers will be under fire.
6 chambers will be cooling and at the same time heating the air required for combustion of fuel.
1 chamber will be empty.

In the ordinary type the fuel is dropped through flues in the roof. If oil is used there is no ash In the Belgian type the fuel is fed by outside grates about 10 ft apart The efficiency of a Hoffmann kiln is fairly high, using only 3 cwt of coal to 1 ton of lime produced The quality of the lime is good but irregular where the ash is mixed with the lime

Qualities and Uses of Lime.—Commercial lime ranges in composition from almost chemically pure calcium oxide to a material closely resembling Portland cement The following analyses illustrate this·

	Buxton lime	Common building lime	Chaux de Teil	Blue Lias lime
Insoluble residue	0·71	13·20	0·62	2·39
Combined silica (SiO_2)		10·34	22·10	14·17
Alumina (Al_2O_3)	0·11	1·64	1·82	6·79
Ferric oxide (Fe_2O_3)				2·34
Lime (CaO)	98·72	51·10	66·72	63·43
Magnesia (MgO)	0·46	1·04	1·17	1·54
Sulphuric anhydride (SO_3)	—	0·21	0·49	1·63
Carbonic anhydride (CO_2)	—	8·00	0·64	3·64
Water (H_2O)	—	14·47	5·36	2·69
Alkalis and loss	—		1·08	1·38
	100·00	100·00	100·00	100·00

As mentioned above, the purest kinds are needed for chemical manufacture, and the less pure varieties, which approach the nature of cement, are generally preferable for building In the case of limes containing so much silica as does Chaux de Teil and so much silica and alumina as does Blue Lias lime, they may be regarded as hydraulic cements rather than limes proper. A rough trade distinction exists between "fat" and "poor" lime. The former is fairly pure and slakes rapidly and with a high rise of temperature; the latter, containing some combined silica and alumina, slakes slowly and relatively feebly. Both, when mixed with sand, form mortars, but fat lime sets only by drying and subsequent adsorption of carbonic acid from the air, whereas the siliceous constituents in poor lime will them

selves set, to some small extent, in the manner of a cement. Ordinarily, however, no such chemical combination takes place and the impurities serve only to depreciate the quality of the lime. Eckel gives analyses of high calcium limes used in America which show 92–99% CaO, while the lean limes contain 81–85% CaO. He also states that limes containing more than 5% impurities will usually be dark in colour, comparatively slow slaking, and difficult to trowel in working. In rural districts of England lime is almost always slaked on the spot where and at the time when it is to be used. On the Continent the lime is usually slaked long before it is used, and is thus allowed to become completely hydrated. This method is now being adopted in England, as shown by the hydrating plant attached to modern kilns. The modern method of preparing hydrated lime is to crush the burnt lime to a coarse powder, the necessary water being added to the whole or to a portion of the lime, the remainder being added later. A pan with agitator or revolving cylinders is used for the hydration and the material is then sieved.

In the Ashmore, Benson, Pease & Co., Ltd., hydrating plant shown in Fig. 4 the process is continuous. The lime passes from the kiln on a conveyor to a hammer crusher, whence it goes by means of a bucket elevator to a hydration plant consisting of five revolving cylinders in which it is thoroughly incorporated with the amount of water required to hydrate the lime. From here it passes through a ring roller and is then elevated to the top of the silos whence it is distributed by means of a belt conveyor to the storage silos.

Lime made from dolomite needs much care in slaking as the hydration of the magnesia takes place slowly and may occur after the mortar is in place, and by expansion cause destruction of the work.

Although lime will not act on sand at the ordinary temperature, it attacks it readily at a moderate temperature. The manufacture of sand lime bricks is dependent on this fact (*see* BUILDING MATERIALS, section VII, p. 48).

Pure calcium oxide forms white porous amorphous masses of sp.gr. 2·3 to 3·08 (3·09 to 3·15, Eckel), highly infusible, melting only in the highest temperature of the oxyhydrogen blowpipe flame or in the electric arc. In the ordinary oxyhydrogen flame it emits an intense light, which is much used for lantern projection.

Calcium oxide has been obtained by Brügelmann in minute cubic crystals of sp.gr. 3·251 by heating the nitrate in a porcelain flask (Ann. Phys. Chem. 1877, [ii], 2, 466; 1878, [ii], 4, 277).

A crystalline mass, found upon the lining of a continuous lime kiln at Champigny after 28 months' continuous work, was also shown to consist of small cubical crystals of pure lime, of sp.gr. 3·32 (Levallois and Meunier, Compt. rend. 1880, 90, 1566).

There is evidence of the existence of two forms of calcium oxide. The oxide obtained by heating calcite at a low red heat is fine grained and porous. When heated at higher temperatures the refractive index increases and cubic crystalline calcium oxide is formed for which $n_D = 1·83$. The melting-point of CaO as determined by the Holborn-Kurlbaum optical pyrometer is 2,570° (Ruff and Schmidt, Z. anorg. Chem. 1921, **117**, 172).

Amorphous lime takes up water with remarkable avidity, forming calcium hydroxide, $Ca(OH)_2$, the combination being accompanied by a contraction in volume and evolution of heat [15·54 kg.-cal. per g.-mol. (Thomsen)], and light (Pelletier, Ann. Chim. 1823, [ii], 23, 217). A rise in temperature of 468° has been recorded by Herzfeld (Z. Ver. deut. Zucker-Ind. 1897, 820). It is used extensively in the laboratory and in works as a drying agent. On exposure to air the amorphous variety of lime rapidly adsorbs water and carbon dioxide; anhydrous lime, however, only adsorbs the gas when heated to near 415°; comparative tests show that carbon dioxide penetrates to a depth of about 3 in. in 20 days. More water is taken up in summer than in winter, but the carbon dioxide adsorption is about the same (Whetzel, Ind. Eng. Chem. 1917, **9**, 287). Lime is readily soluble in dilute mineral acids. It also reacts with ethyl alcohol when heated in a sealed tube to 115°–125°, giving a mixture of hydroxide and ethoxide of calcium.

Calcium Hydroxide, or *Hydrate of Lime*, $Ca(OH)_2$, is obtained by slaking fresh, well-burnt quicklime with about a third of its weight of water. It forms a white amorphous powder of sp.gr. 2·078, sparingly soluble in water, and less so in hot than in cold water, as seen from the following table (A. Guthrie, J.S.C.I. 1901, **20**, 223):

100 c.c. saturated limewater contains:

Temperature. °C.	CaO in grams.	Temperature. °C.	CaO in grams.
5	0·1350	40	0·1119
10	0·1342	50	0·0981
15	0·1320	60	0·0879
20	0·1293	70	0·0781
25	0·1254	80	0·0740
30	0·1219	90	0·0696
35	0·1161	100	0·0597

Sodium hydroxide decreases the solubility. d'Anselme (Bull. Soc. chim. 1903, [iii], **29**, 936) gives the following data:

Temp. °C				
	0·00	0·400	2·666	NaOH g. per litre.
20	1·17	0·94	0·39	CaO g. per litre.
50	0·88	0·65	0·20	CaO g. per litre.
70	0·75	0·53	0·11	CaO g. per litre.
100	0·54	0·35	0·05	CaO g. per litre.

The solution known as limewater has an alkaline reaction, and absorbs the carbon dioxide of the atmosphere, forming a pellicle of calcium carbonate. Limewater of definite strength for pharmaceutical purposes is best prepared by using freshly ignited lime. In preparing limewater from ordinary lime, the first solutions should invariably be rejected, as they will contain nearly all the soluble salts

of the alkalis and the baryta and strontia present in the lime as impurities. Milk of lime is a suspension of calcium hydroxide in less water than is required for its complete solution. Calcium hydroxide is much more soluble in solution of sugar than in pure water due to the formation of soluble saccharates (for solubilities *v.* Weisberg, Bull. Soc. chim 1899, [iii], 21, 773, *see also* Bassett, J C.S. 1934, 1270)

Calcium hydroxide is precipitated by potassium or sodium hydroxide from strong solutions of the chloride, using highly concentrated solutions a solid product may be obtained

Ashton and Wilson (Amer. J. Sci 1927, (v), 13. 209) obtained crystals of calcium hydroxide by various methods showing always the same form and refractive indices The crystals belong to the hexagonal system and occur as short hexagonal prisms or plates with perfect cleavage parallel to the (0001) face. The refractive indices are $\omega=1\ 574\pm0\ 003$, $\epsilon=1\ 545\pm0\ 003$ for sodium light, birefrigence is 0 029, d_4^{20} 2 230±0 005 interference figure is uniaxial negative The lattice constants are $a_0=3\ 579$, $c_0=5\ 0280$ Å, the unit cell contains 1 molecule.

Selivanoff (J Russ Phys Chem Soc 1912, 44, 1797; 1913, 45, 257) states that hydroxides obtained by slaking specimens of different origin all agree closely in composition with the formula $Ca(OH)_2$. The hydroxide adsorbs water which is largely lost in a desiccator over $CaCl_2$ or H_2SO_4 Supersaturated solutions were found to contain 0 260–0 264 g of CaO per 100 c.c, agreeing with Guthrie The hydroxide $Ca(OH)_2$ may be obtained in hexagonal plates or prisms by heating supersaturated solutions of lime or by evaporating an aqueous solution under diminished pressure at 28°–30°. The cryohydrate of lime forms on solidification a transparent ice, when this melts it deposits elongated hexagonal plates or rhombic plates of the hydrate, $2Ca(OH)_2,H_2O$, which is very unstable

Calcium hydroxide is an energetic base combining with acids to form salts and displacing ammonia from its compounds

At a red heat, calcium hydroxide is decomposed, water being driven off and oxide remaining.

Slaked lime is used extensively in the preparation of mortars and cements (*v* BUILDING MATERIALS, section III, p. 129), for softening hard waters, in the preparation of lyes for the defecation of sugar, and for agricultural purposes. As regards the application of lime to the soil, only a small proportion reappears as carbonate, the remainder being adsorbed by the soil constituents.

The slaking properties of lime depend to a great extent on its source, which determines the looseness of the powder. Samples made from oxalate and nitrate are exceptionally dense. Calcium chloride and sodium chloride in the slaking water accelerate the slaking, sodium hydroxide retards it (Kohlschutter and Feitknecht, Helv. Chim. Acta, 1923, 6, 337)

Calcium Dioxide, CaO_2, was first prepared by Thénard by the action of excess of hydrogen peroxide upon limewater, when microscopic quadratic plates of the composition $CaO_2,8H_2O$, sparingly soluble in water and insoluble in alcohol, were precipitated. According to Conroy (J.C S 1873, 26, 810), the peroxide is most conveniently prepared by adding limewater in considerable excess to an aqueous solution of sodium peroxide acidified with nitric acid. It is also obtained as a finely divided white precipitate on adding a neutral or alkaline solution of sodium peroxide to a solution of a calcium salt CaO_2 in the anhydrous form (Riesenfeld and Nottebohm, Z anorg. Chem 1914, 89, 405) separates from very concentrated solutions near 0°, and above 40° even from very dilute solutions. The octahydrate is obtained from very dilute solutions at the ordinary temperature The crystals are isomorphous with those of hydrated barium peroxide. On exposure to air they effloresce, and when heated to 100° are converted into the anhydrous peroxide. On increasing the heat, half the oxygen is driven off, leaving a residue of pure lime There is no appreciable decomposition below 220°. Up to 273° decomposition is slow, but then becomes very rapid. Finely divided CaO_2 decomposes explosively when heated rapidly to 275°. The dissociation pressure at 255° is more than 190 atmos (Reisenfeld and Nottebohm, Z. anorg Chem 1914, 90, 37)

Calcium Tetroxide, CaO_4 By warming calcium peroxide octahydrate with 5–6 times its quantity of pure H_2O_2 (30%) until evolution of oxygen ceased, and then washing with water, alcohol and ether, Traube and Schulze (Ber 1921, 54, (B), 1626) obtained a compound possessing a bright yellow colour which can be heated to 130° without change It shows the property of dissolving in acid with evolution of oxygen and production of H_2O_2 The quantity of the oxygen from the best preparations was 2 7% by weight of the substance. The evolved oxygen is inactive, and as the compound is stable towards heat it is assumed to be the tetroxide CaO_4 which is present to a maximum extent of 8 7%, the remainder being chiefly calcium peroxide with a little carbonate.

Calcium Chloride, $CaCl_2$, is found in the water of many springs and rivers, and is a constituent of the saline matter dissolved in sea water. Calcium chloride likewise occurs, together with magnesium chloride and alkaline chlorides in the tachydrite and carnallite of the Stassfurt deposits, tachydrite containing 21% $CaCl_2$ and 36% $MgCl_2$, while carnallite contains 3% $CaCl_2$ and 31% $MgCl_2$. It occurs as a major constituent of Dead Sea brine (*v.* BROMINE, p. 108).

Calcium chloride may be obtained by passing chlorine over the red hot oxide, or by dissolving lime, chalk or marble in hydrochloric acid and evaporating. If it is necessary to obtain the salt pure, chlorine water may be added to the solution in hydrochloric acid in order to oxidise any iron present, which may then be precipitated by the addition of milk of lime, and filtered off The slightly alkaline filtrate is then acidified with hydrochloric acid and evaporated to the crystallising point.

Calcium chloride is obtained in large quantities as a by-product in many manufacturing processes, notably in the preparation of potassium

chlorate and in the manufacture of sodium carbonate by the ammonia-soda process; it may be obtained in the pure state from these crude products by the method just indicated. Many attempts were made to recover the chlorine of the waste product; hydrochloric acid so produced, however, could not compete with that obtained by the direct process.

Saturated solutions of calcium chloride deposit the hydrated salt, $CaCl_2,6H_2O$, in large hexagonal prisms terminated by pyramids. The crystals melt at 29° in their water of crystallisation and deliquesce rapidly in the air, forming a viscous fluid, formerly termed *oleum calcis*. Heated below 200°, or in a vacuum over sulphuric acid, the crystals lose 4 molecules of water. The remaining 2 molecules can only be expelled above 200°. According to Weber (Ber. 1882, **15**, 2316), the salt dried at 180°–200° is practically anhydrous, containing only 0·2% of water. Besides the two hydrates above described, Lescœur (Compt. rend. 1881, **92**, 1158), from determinations of vapour tensions of solutions, shows the probable existence of two others, $CaCl_2,4H_2O$ and $CaCl_2,H_2O$. The tetrahydrate, however, can only exist below 129°. Milikan (Z. physikal. Chem. 1917, **92**, 496) has examined the equilibrium conditions in the system $CaCl_2$–HCl–H_2O. The solution containing 44·5% $CaCl_2$ and 3·3% HCl is in equilibrium with the solid phases $CaCl_2,6H_2O$ and $CaCl_2,4H_2O$, and the solution containing 28·48% $CaCl_2$ and 21·40% HCl with the solid phases $CaCl_2,4H_2O$ and $CaCl_2{\cdot}2H_2O$.

Anhydrous calcium chloride is a white porous mass, which fuses at a red heat or, according to Schaeffer (Jahrb. Min. Beil.-Bd. 1919, **43**, 132) at 773°. On cooling the salt solidifies to a translucent mass of crystals of sp.gr. 2·205. The crystal structure of calcium chloride has been investigated by A. K. van Bever and W. Nieuwenkamp (Z. Krist. 1935, **90**, 374). By cooling fused dehydrated $CaCl_2$ slowly in vacuum single crystals were obtained having rhombic pseudotetragonal structure, a_0 6·24, b_0 6·43, c_0 4·20 Å, space-group *Pnnm*. A powder photograph does not agree with this structure but corresponds with a second modification, arising from the first by mechanical disturbance. A slight decomposition into oxide and carbonate occurs when the fusion is performed in air. On this account the porous chloride obtained by drying the crystals at 260° is better adapted for desiccating purposes, especially for the adsorption of water in organic analysis. McPherson (J. Amer. Chem. Soc. 1917, **39**, 1317) has shown that granular calcium chloride which has been heated at 260°–275° in a current of air dried over phosphoric oxide will remove every trace of moisture from a gas passed over a sufficiently long column of the salt. If the fused mass is exposed to the sun's rays it becomes phosphorescent in the dark, and was formerly called Homberg's phosphorus, after the discoverer of the fact in 1693.

Anhydrous calcium chloride is highly deliquescent: 100 parts of the powder exposed to an atmosphere saturated with aqueous vapour absorbed 124 parts of water in 96 days. According to Kremers (Pogg. Ann. 1858, **103**, 57; 1858, **104**, 133; J., 1858, 40), the following quantities of water are required to dissolve one part by weight of the anhydrous salt:

At 10·2°	20°	40°	60°
1·58	1·35	0·83	0·72

The following table shows the densities at 20°/4° of calcium chloride solution (Internat. Critical Tables, 1928, iii, 72).

$CaCl_2$%.	Density.	$CaCl_2$%	Density.
2	1·0148	16	1·1386
4	1·0316	18	1·1578
6	1·0486	20	1·1775
8	1·0659	25	1·2284
10	1·0835	30	1·2816
12	1·1015	35	1·3373
14	1·1198	40	1·3957

A solution of 50 parts anhydrous $CaCl_2$ in 100 parts water boils at 112°, one containing 200 parts boils at 158°, and one containing 325 parts boils at 180°.

According to Lefebvre (Compt. rend. 1870, **70**, 684) a supersaturated solution of calcium chloride is formed by dissolving 350–400 g. of the crystallised salt in 50 c.c. warm water or 200 g. of the anhydrous salt in 250 c.c. water; it may be shaken after cooling without crystallisation, but solidifies on contact with a crystal of the salt. If cooled to 5·8°, this solution begins to crystallise, the temperature rising to 28°–29°. A solution containing 55% $CaCl_2$ deposits at about 15° large plates of the tetrahydrate, $CaCl_2,4H_2O$, which do not induce the crystallisation of the supernatant liquor. This solution, in passing from liquid to solid state, undergoes at 70° a contraction 0·0832 of its volume.

The crystallised chloride $CaCl_2,6H_2O$ also deliquesces rapidly, and dissolves in half its weight of water at 0°, in one-fourth its weight at 16°, and in all proportions of hot water. In dissolving it absorbs heat, while the anhydrous chloride dissolves with evolution of heat. A mixture of 1·44 parts crystallised chloride with 1 part of snow reduces the temperature to −54·9°, more than sufficient to freeze mercury.

Both the anhydrous and hydrated chloride dissolve readily in alcohol, 10 parts at 80° dissolving 6 parts anhydrous $CaCl_2$; on evaporation in a vacuum at winter temperature, rectangular plates of $2CaCl_2,7C_2H_6O$ are deposited.

Potassium and calcium chloride mixtures have a maximum m.p. at 740° with equal molecules of the two chlorides and two minima at 630° with 85% $CaCl_2$ and 40% $CaCl_2$, the former being the eutectic point for $CaCl_2,KCaCl_3$ and the latter for $KCl,KCaCl_3$ (Moldenhauer and Andersen, Z. Elektrochem. 1913, **19**, 344, 447).

Calcium and barium chlorides form a double salt $CaCl_2,BaCl_2$ (m.p. 631°), but no mixed crystals. There is a eutectic point at 602° with 38 mols. % $BaCl_2$. Calcium and strontium chlorides form a continuous series of mixed crystals with a minimum at m.p. 658° with 66 mols. % of $CaCl_2$. Barium and strontium chlorides are also completely miscible. The ternary diagram is divided into areas of com-

plete and incomplete miscibility by a limiting curve. The ternary mixed crystals separating in the area of complete miscibility are dimorphous. In the ternary area the existence of the binary compound, $CaCl_2,BaCl_2$, crystallising at 631°, and of a ternary compound, $CaCl_2,BaCl_2,SrCl_2$, crystallising at 500°, was established (Schaefer, Jahrb. Min. Beil.-Bd. 1919, 43, 132)

Calcium chloride forms a continuous series of solid solutions with strontium, cadmium, and manganous chlorides, the melting-point curve in each case having a minimum which occurs at 646°, 545°, and 583° respectively. Mixtures of $CaCl_2$ with $BaCl_2$ and with $PbCl_2$ form a simple eutectic series, the eutectic points being at 600° and 35 mols % $BaCl_2$ and at 468° and 83 mols % $PbCl_2$ respectively (Sandonnini, Atti R. Accad. Lincei, 1911, (v), 20, ii, 496–646)

Anhydrous calcium chloride adsorbs ammonia gas, forming the compound $CaCl_2,8NH_3$ as a white powder, which, on exposure to air, solution in water, or on heating, is decomposed. Thrown into chlorine gas, the compound takes fire.

Calcium Oxychloride,

$$3Ca(OH)_2,CaCl_2,11H_2O.$$

(V I Nikolaev and S. A Glinskich, Compt. rend. Acad Sci. U.R.S.S 1934, 1, 572) The erroneous formula attributed to this compound by Ditte (Z anorg Chem 1893, 3, 34), Schreinemakers and Figee (Chem. Weekblad 1911, 8, 683) and Milikan (Z. physikal Chem 1917, 92, 59) was due to the fact that the crystals contained up to 16% of mother liquor

When calcium chloride is fused at a bright red heat in a current of moist air, it is gradually converted to an oxychloride of the composition $CaCl_2,CaO$, and eventually to the oxide (Gorgeu, Compt rend. 1884, 99, 256).

B Neumann, C. Kroger, and H. Juttner (Z. Elektrochem 1935, 41, 725) record equilibrium data for the system $CaCl_2$–CaO (600°–1,300°) The existence of $4CaCl_2,CaO$ has been established. Steam begins to decompose $CaCl_2$ at 780°. The reactions have been studied over a range of temperature and are discussed in relation to the equilibrium diagrams

Calcium Hypochlorite *v.* BLEACHING POWDER.

Calcium Chlorate, $Ca(ClO_3)_2$, is produced when chlorine is passed into hot milk of lime, but is difficult to separate from the chloride simultaneously formed; the reaction is usually represented as follows:

$$6Ca(OH)_2+6Cl_2 = Ca(ClO_3)_2+5CaCl_2+6H_2O$$

According to Lunge (J S C.I. 1885, 4, 722), the reaction really takes place in several stages, calcium hypochlorite and hypochlorous acid being first formed and mutually reacting with production of calcium chlorate:

$$(1)\ Ca(OCl)_2+2Cl_2+2H_2O=CaCl_2+4HClO$$

$$(2)\ 2Ca(OCl)_2+4HClO= CaCl_2+Ca(ClO_3)_2+2Cl_2+2H_2O$$

The free chlorine serves only as carrier of the oxygen of two molecules calcium hypochlorite to a third molecule of the hypochlorite which is oxidised to chlorate. Lunge's experiments show that the best mode of converting hypochlorite into chlorate is to raise the temperature of the solution, while maintaining a slight excess chlorine The heat produced by the reaction on the large scale is sufficient.

A yield of nearly 90% of calcium chlorate can be prepared by the electrolysis of a 10% solution of calcium chloride. The density of the current should be 10 amperes per square decimetre at the anode and double at the cathode; temperature 50° (Bischoff and Foerster, Z. Elektrochem 1898, 4, 464).

It may also be prepared by precipitating potassium chlorate with calcium silico-fluoride It crystallises in deliquescent rhomboidal plates, very soluble in water and alcohol; the crystals contain 16 5% water, melt when warmed, and decompose on further heating

Calcium Perchlorate, $Ca(ClO_4)_2$, may be obtained by saturating perchloric acid with caustic lime It is extremely deliquescent and crystallises in prisms soluble in alcohol.

Calcium Bromide, $CaBr_2$ (m p. 730°), is formed by heating calcium in bromine vapour, or by dissolving lime or calcium carbonate in hydrobromic acid and evaporating. The silky needles thus obtained are hydrated, but may be converted to the anhydrous salt by heating Calcium bromide much resembles the chloride in properties, being deliquescent and very soluble in alcohol $NaBr$ and $CaBr_2$ solidify to form two series of solid solutions with a eutectic point at 513°, and on further cooling a reaction takes place at 469°, a compound $NaBr_2,2CaBr_2$ being formed KBr forms a single compound $KBr,CaBr_2$, represented by a maximum on the freezing-point curve at 637°. There are eutectic points at 544° and 563° respectively (Kellner, Z. anorg. Chem. 1917, 99, 137)

Calcium Iodide, CaI_2, may be prepared by combustion of calcium in iodine vapour, or by solution of lime or the carbonate in hydriodic acid and evaporating and fusing the residue in a closed vessel; or hydriodic acid prepared from red phosphorus and iodine may be made slightly alkaline with milk of lime and yields a solution of calcium iodide (Liebig Annalen, 1862, 121, 222). Heated in contact with air, it fuses below a red heat, and is decomposed with liberation of iodine vapours and formation of lime.

The iodide of calcium and silver of the composition $CaI_2,2AgI,6H_2O$ has been prepared by Simpson (Proc. Roy. Soc. 1878, 27, 120) by saturating a hot concentrated solution of CaI_2 with moist silver iodide. It crystallises on cooling in long white needles, decomposed by water. The basic salts formed by the alkaline earth metal haloids have been studied by the equilibrium relations in the ternary system between the haloids, the corresponding hydroxides, and water. The basic salt $CaI_2{\cdot}3CaO,16H_2O$ is stable at 25° in contact with solutions containing 28 44% to 66 68% of CaI_2 (Milikan, Z. physikal. Chem. 1917, 92, 59).

Calcium Iodate, $Ca(IO_3)_2,6H_2O$, is obtained by crystallising mixed solutions of potassium iodate and calcium chloride. The hydrated salt forms four sided prisms which effloresce in the

air, and become anhydrous when heated to 200°. From a solution acidified with nitric acid, it separates in trimetric crystals. The crystals are soluble in 454 parts water at 18°, and in 102 parts of boiling water, but are insoluble in alcohol. The anhydrous salt gently heated in a porcelain retort evolves 14·78% of oxygen and 54·07% of iodine, leaving 31·14% of a residue rich in pentabasic periodate of calcium. Heated more strongly, it evolves more oxygen and iodine, and leaves 20·35% of a mixture of pentabasic periodate and free lime. Calcium iodate detonates violently when heated on charcoal.

Sonstadt proposed (B.P. 6304/84) to use calcium iodate as an antiseptic.

Calcium Periodate, $Ca(IO_4)_2$, is obtained by dissolving calcium carbonate in a strong solution of periodic acid and evaporating the acid solution over concentrated sulphuric acid. By treating feebly acid solutions with calcium carbonate, or by the action of an alkaline periodate on calcium nitrate a basic salt $Ca(IO_4)_2{\cdot}CaO,9H_2O$ or $3H_2O$, is formed (Rammelsberg, Jahresber. 1868, 164; Langlois, Ann. Chim. Phys. 1852, [iii], 34, 257).

Calcium Fluoride, CaF_2, is found widely distributed in nature and is known as fluorspar. It is the only common mineral in which fluorine forms one of the principal constituents. It occurs both massive and in beautiful crystals, generally cubes or forms in combination with the cube. It is a common vein mineral, occurring usually in association with metallic ores, barytes, calcite, etc. It presents a variety of colours, sometimes shading into one another as in the beautiful "Blue John" of Derbyshire. There is a considerable industry carried on in fluorspar districts in the carving of ornamental vases and other articles, the brilliantly coloured varieties being especially in demand. While being heated fluorspar phosphoresces in the dark. All the coloured specimens lose their colour on heating, green specimens being the most difficult to decolourise completely. Thermoluminescence is very marked in all naturally coloured crystals, a violet light being emitted in most cases, with decrepitation. Free fluorine has been shown to exist in a dark violet fluorspar from Quincié, Dept. du Rhône. Crystallised colourless fluorspar can be coloured deep blue by the β- and γ-rays of radium, and then shows on gentle warming a beautiful green thermo-luminescence which fades and changes into the pale violet light characteristic of all fluorspars. Debierne found that certain dark violet fluorspars smell of ozone. When heated they lose their colour and thermo-luminescence and also yield helium in variable but small quantity. On exposure to radium rays the violet colour is restored. Calcium fluoride is a constituent in small quantities of many plant ashes, of bones, and of the enamel of teeth. When the gelatinous calcium fluoride obtained by precipitating any soluble calcium salt with fluorides of sodium or potassium, is heated with water slightly acidified with hydrochloric acid it is transformed into microscopic octahedral crystals.

Calcium fluoride is soluble in about 2,000 parts of water at 15°, and is slightly more soluble in water containing carbon dioxide. It dissolves in hydrofluoric acid and in strong hydrochloric acid, and is precipitated in the gelatinous form by ammonia. It is fusible at 1360°, and is used as a flux in many metallurgical operations, especially in the reduction of aluminium.

Calcium fluoride is not insoluble in acetic acid as generally supposed. Acetic acid $0{\cdot}5N$ dissolves at 40°, 0·153 g.; at 60°, 0·178 g.; at 80°, 0·206 g.; at 100°, 0·229 g. per litre. The corresponding figures for N-acid are 0·175, 0·203, 0·237, 0·264, and for $2N$-acid 0·192, 0·229, 0·267, and 0·300 (Duparc, Wenger, and Graz, Helv. Chim. Acta, 1925, 8, 280).

S. Nagai and M. Miyasaka (J. Soc. Chem. Ind. Japan, 1934, 37, 303–306B) show that the addition of CaF_2 to mixtures of $CaCO_3$ or CaO with SiO_2 lowers the temperature of combination by about 200° and diminishes the proportion of CaO in the silicate when heating is prolonged. The presence of increasing amounts of CaF_2 increases the rate of the reaction $2CaO+SiO_2 \rightarrow 2CaO,SiO_2$ at *1,200°*; at 1,300° the conversion produces some $3CaO,SiO_2$. Part of the CaF_2 is removed by volatilisation during the reaction (*ibid.* 419).

Calcium fluoride is decomposed at a high temperature by water vapour into lime and hydrofluoric acid. Fusion with alkaline carbonates or hydroxides yields carbonate or oxide of calcium and alkaline fluorides. It is decomposed on gently warming with strong sulphuric acid into calcium sulphate and hydrogen fluoride. At a red heat it is also decomposed by chlorine.

Calcium Carbide, CaC_2.—Maquenne, in 1892, prepared calcium carbide as an impure amorphous black powder, and Travers obtained it by heating together calcium chloride, sodium and carbon. It was not, however, until the advent of the electric furnace that it became possible to manufacture a pure carbide suitable for the preparation of acetylene. Moissan (Compt. rend. 1904, 138, 243) heated a mixture of lime 120 g., sugar carbon 70 g., in the crucible of an electric furnace for 20 minutes with a current of 350 amperes and 70 volts. At the temperature of liquefaction of the lime calcium carbide was formed according to the equation :

$$CaO+3C=CaC_2+CO$$

Botolfsen (Ann. Chim. 1922, 18, 5) shows that pure calcium carbide is not obtained by heating calcium acetylide-acetylene-ammonia,

$$C_2Ca,C_2H_2,4NH_3,$$

as stated by Moissan. The product treated with water gave a mixture of hydrogen, ammonia, and acetylene. The reaction between metallic calcium and free carbon is not appreciable below the melting-point of the metal. Above 800° combination takes place more rapidly if the calcium is in the state of vapour. When the carbide is prepared in an iron tube the product, even when practically pure, is black, the coloration being due not to free carbon but to iron. Calcium carbide dissociates on heating into its elements without any intermediate formation of a sub-carbide; dissociation is influenced by the presence of iron, iron oxide, and other substances.

Ruff and Foerster (Z. anorg. Chem. 1923, 131, 321) attempted to make the pure carbide by softening the commercial carbide (74.9% CaC_2) in hydrogen at 2,000°–2,100° and squeezing out the carbide with a carbon rod, the process being repeated on the expressed material. Ruff and Josephy (Z. anorg Chem 1926, 153, 17) made a pure carbide from calcium prepared by distillation of commercial calcium *in vacuo* at 1,500°. The preparation of the carbide from the metal and a pure soot was done in an iron crucible in an argon atmosphere at 1,250°, nitrogen being first removed by heating the calcium *in vacuo*

The product obtained in an open crucible is always of a loose nature and very sensitive to moisture, but by careful remelting in argon at 780 mm it is obtained as a greyish black crystalline mass (Ruff and Foerster, *l.c.*).

System Calcium Carbide–Lime.—Vaporisation of calcium carbide in nitrogen at 1,100° yields calcium cyanamide, which vaporises with partial decomposition at about 1,300°. When heated in hydrogen traces of acetylene are found above 2,200°, and in carbon monoxide calcium oxide and carbon at 1,700° From the curves representing these processes, the dissociation pressure of calcium carbide was found to be 1 atm. at 2,500°±50°, *i e.* 1 mm. at 1,825°±50°. Pure calcium carbide melts at about 2,300°. The equilibrium of the reaction

$$CaO\text{ (liquid)}+3C=CaC_2\text{ (liquid)}+CO$$

depends on the partial pressure of carbon monoxide as well as on the ratio (CaC_2) to (CaO). In an atmosphere of carbon monoxide when the eutectic solidifies the reaction is rapidly and completely reversed, but preparation of pure carbide was not realised experimentally on these lines (Ruff and Foerster, *l c.*).

R. Taussig states that commercial carbide always contains a certain amount of lime, the amount varying with the temperature employed.

G. Flusin and C. Aall (Compt. rend. 1935, 201, 451) have investigated the fusion point diagram of the system CaC_2–CaO in presence of traces of SiO_2, Fe_2O_3, Al_2O_3, MgO, C, and SO_3, and find eutectics at 68% of CaC_2 (1,750°) and at 35.6% of CaC_2 (1,800°), with a maximum at 52.5% of CaC_2 (1,980°) corresponding with the compound CaC_2,CaO.

Calcium carbide reveals cleavage surfaces nearly equal and parallel to three directions at right angles to one another. A cleavage plate shows that it contains thin lamellæ parallel or inclined at 45° to the cleavage plate. It is considered to be orthorhombic with polysynthetic twinning (Warren, Amer. J. Sci. 1921, 3, 120).

Accurate X-ray investigation by the Weissenberg-Bohm method has shown that calcium carbide crystals are tetragonal. The rectangular pieces split from the carbide consist of small crystals which give a wrong form of X ray diagram. There is a coalescence of three faces, the *c* axes of which lie at right angles to each other in three directional space. The unit cell contains 4 mols. and the calculated density is 2.21, in good agreement with the experimental value of 2.1. The calcium atoms are disposed in a face-centred lattice and the carbon atoms form two faced centred lattices (von Stackelberg, Naturwiss. 1930, 18, 305–306).

Pure calcium carbide is crystalline, colourless and transparent, but the commercial variety, discoloured by iron, is usually brownish red. Its characteristic reaction is the decomposition of water in the cold, with the liberation of acetylene and the formation of calcium hydroxide (*v* ACETYLENE).

Calcium Carbide, Manufacture of.—The commercial manufacture of calcium carbide is credited to Willson in America and Héroult in Europe It was started in the early eighties of last century, and by progressive development acquired the distinction of being the largest consumer of energy in the electric furnace industry This continued extension resulted in a better design and increased size of furnace, together with the necessary equipment for handling large quantities of raw materials and for preparing the carbide for the market.

The chief factors which have to be considered in the choice of a site for a carbide factory are supplies of raw material consisting of limestone, and coke or anthracite, and an abundant source of cheap electric power Large works have consequently been established in places where a practically unlimited supply of water power is available Hence, most progress in the industry has been witnessed in Norway and Sweden, where—excepting coal—other demands are amply satisfied.

The raw materials used in the manufacture of calcium carbide should be as pure as possible. Special attention should be paid to obtaining them free from phosphorus, sulphur or magnesia; silica, iron or alumina should be present only in small quantities (*v* Witherspoon, J.S.C.I. 1913, 32, 113)

Phosphorus occurs in limestone as calcium phosphate, and is reduced at the temperature of the furnace and in the presence of carbon, to calcium phosphide, which, when brought into contact with water, evolves phosphoretted hydrogen; this impurity in acetylene used for illuminating purposes causes a haze of phosphorus pentoxide, which is very objectionable. So carefully, however, are the raw materials selected that all commercial carbides are practically free from phosphorus, the average PH_3 content in acetylene being less than 0.002%. (For a method of examining commercial carbide for calcium phosphide based on that of Lunge and Cedercreutz, *see* Dennis and O'Brien, Ind. Eng. Chem. 1912, 4, 834.)

Sulphur, unless present with considerable amounts of alumina, has little influence on the resulting carbide. Calcium sulphide, formed in the furnace by the reduction of calcium sulphate, does not decompose in the production of acetylene, but in the presence of alumina, aluminium sulphide may be formed, which yields hydrogen sulphide when brought in contact with water. Very little trouble, however, is experienced with sulphur, as the lime and coal used in the manufacture rarely contain a prohibitive quantity.

Magnesia has the peculiar property of interfering with the formation of calcium carbide in the furnace. If more than 1% of magnesia be present in the lime and coal, the electrical energy required becomes noticeably so much greater that raw materials containing such impurity are considered unfit for use. A flux of fluorspar has been used to counteract this effect, but with little success. Magnesia mixed with carbon and heated in the electric furnace is highly infusible and does not form a carbide; under similar conditions barium and strontium oxides form carbides with ease.

Silica, iron oxides and alumina form silicates, aluminates, and ferro-silicon, which reduce the purity of the carbide and the output of the furnace.

The preparation of the raw materials in carbide manufacture is of much importance, owing to the high temperatures employed in the reduction of the lime. Water in the free state in the coal, or combined as hydroxide in the lime, should be entirely eliminated, its presence reducing the output of the furnace to a very serious extent. The coal (anthracite) or coke is, therefore, thoroughly dried at a low heat in some convenient type of oven or rotary drier. The limestone, consisting of calcium carbonate, requires a high temperature to drive off the carbon dioxide, and the operation is usually conducted in some type of lime kiln fired by coal or gas—the Alby works at Odda used producer gas-fired kilns—or the limestone may be burnt in specially constructed chambers using gases evolved from the manufacture of the carbide. The ingredients were formerly ground fine to ensure a uniform product, but this is now found unnecessary, and the lime is reduced by crushers to 1–2 in. size, and the coal to $\frac{1}{4}$–$\frac{1}{2}$-in. mesh. They are then weighed and mixed roughly in about the theoretical proportions or approximately 100 parts by weight of lime to 65 parts by weight of the carbon content of the coal.

The types of electric furnaces which have been used in the manufacture of carbide may be roughly divided into the intermittent and the continuous forms. The first and earlier type was known as the ingot furnace, as the carbide was allowed to solidify in the crucible.

In practice 4 tons of raw material were handled to produce 1 ton of carbide, and the process was also unsatisfactory on account of the varying quality of the product, which, though pure carbide in the centre, was only a fritted mixture of lime and coke on the crust. In order to improve both the quality and output the American makers adopted a rotating furnace, of which the Horry furnace is the best-known type.

In Europe the early pot furnace was soon changed to a tapping furnace in which the carbide was heated until sufficiently fluid to be run into cast-iron moulds. The earlier furnaces were similar in form to the pot furnace, with one suspended electrode, but it was difficult to get the desired temperature and fluidity. Two or more electrodes were then introduced, and the progress in electric furnace design for high temperatures followed largely its development in the carbide industry. The furnace, as constructed by Alby in Sweden, used a single phase alternating current of 1,500 kilowatts, and produced 50–60 tons of carbide per week.

The electrodes, which in the early days of the industry were obtainable only in comparatively small sizes, could later be purchased up to 22 in. square and more, and an assembly of smaller ones was also used by some manufacturers. The working temperature in the furnace attained 3,000°C., with a somewhat lower casting temperature. To withstand such a great heat the furnace, which is constructed of steel frame-work and plates, has to be lined with some refractory material, preferably as inert as possible towards the elements of the charge, and, where the heat is most intense, cooling tubes may be built into the lining. It is necessary also to insulate the electrodes to prevent short circuiting through the furnace construction, as also to make a gas-tight joint where the closed form of furnace is employed.

Considerable progress has been made in attaining size and efficiency by the use of multiphase current, which has resulted in advantage not only to the carbide industry but also in the manufacture of ferrosilicon and other ferroalloys. According to Helfenstein and Taussig (Seventh Congress of Applied Chemistry), the largest power consumption possible with a built-up electrode amounts to 2,500–3,000 kw., the current being 30,000–40,000 amperes at 75–95 volts at the electrode. In a three-phase furnace—the only type formerly used for large units—this means a total power consumption of from 7,500 to 9,000 kw., or 10,000 to 12,000 h.p. In the manufacture of carbide a further step has been taken in the construction of double three-phase furnaces, in which—in the same hearth—six instead of three electrodes are employed, connected to two separate three-phase units; the power required being from 15,000 to 18,000 kw., corresponding to a production of from 80 to 110 tons of carbide in 24 hours. In this modification there is no increase in loading, but it is interesting as showing that the power capacity so attainable is unlimited, whereas any attempt to increase the power of consumption beyond 2,500 or 3,000 kw. per electrode is found to be impracticable unless the furnace is operated by entirely special methods, as in the Miguet furnace (v. *infra*).

In open furnaces the heat, due to the burning of the gaseous products of the reaction, is so great that even with less than 3,000 kw. per electrode special protection against the heat has to be provided both for the workers and the electrical plant. Simultaneously the gases evolved become a serious nuisance in open carbide furnaces, and smoke is developed disproportionately as the power is increased, for which reason it is not advisable to exceed 3,000 kw. per electrode. Another obstacle to the use of higher concentration of power is the difficulty of satisfactorily charging the raw materials into the furnace so as to keep the electrodes uniformly covered, any undue exposure leading to fuming or distillation of material due to overheating.

As the capacity of the furnace is increased the

utilisation of the gases produced by the reaction becomes of greater economic moment. In the carbide furnace 70–85% of the gases is carbon monoxide, with carbon dioxide and water as the sole impurities, and these are easily removable in practice Furnaces are now designed entirely closed in, so that evolved gas can be utilised for heating purposes, and by so doing smoke nuisance and excessive radiation of heat are avoided.

The type of furnace as covered by Helfenstein's patents illustrates the main features of interest in connection with mechanical charging and other general problems of management of the electrical furnace for the manufacture of carbide. Fig. 5 shows an elevation and section of an 8,000–10,000 kw. single three phase furnace About 8–10 m. above the bottom plate is a charging floor, where the raw material is brought to the charging apparatus at regular intervals, as in blast furnace plants, by tipping waggons. The charging arrangements consist of a large mixing chamber, which can be closed gas tight, communicating with the body of the furnace, through which the central hanging electrode, of 3,000–4,000 kg. weight, passes, being thus surrounded on all sides by the mixture. As the material is used, in the process the mixing reservoir, which has a capacity of from 5,000 to 7,000 kg, is fed continuously through large pipes from the charging floor above. Wide slits provided with gas tight covers are made in the top of the furnace proper, near the mouth of the reservoir, for observation and control of the process.

When no more profitable use of the waste gases is available, their immediate application in preheating the charge can be carried out as illustrated in Fig. 5. It is seen that in the upper part of the hearth there is a gas filled corner

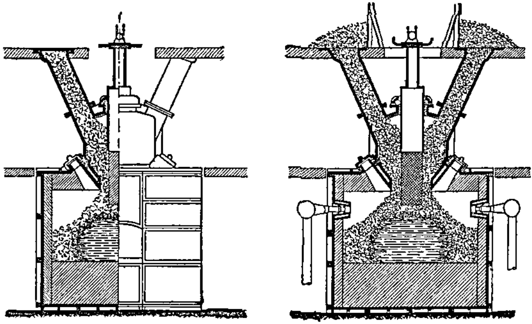


FIG. 5.

space bounded by the naturally sloped surface of the raw materials; by blowing or sucking air in at the nozzles, as indicated in the figure, this space is converted into a combustion chamber, the gases burning in contact with the mixture of material in the hearth. In another Austrian modification the furnace is provided with charging vessels in the form of shafts similar in design to Helfenstein's, but with a branch for taking off the waste gases.

The works of the A.-G. fur Stickstoffdunger near Cologne, described by Allmand and Williams (J.S.C.I. 1919, 38, 304R), were capable of producing 200 tons of carbide a day, the power being obtained from five three-phase turbo-generators of 11,250 kw. each, and three smaller ones capable of supplying power and current for seven furnaces.

Most of the calcium carbide of Europe is now manufactured from hydro-electric power in Norway and Sweden. The process is described in "Die Industrie des Kalziumkarbides," by Rudolf Taussig, Wien, Verlag von Wilhelm Knapp, Halle, 1930.

Two types of furnace are in use, depending upon whether one phase or three phase current is employed The three phase furnace is generally elliptical in shape with axes of 4·2 m by 8 m. and 3 7 m. deep, and is similar in other respects to the arrangement already illustrated in Fig. 5.

The latest type given by Taussig is a one-phase furnace designed by Miguet.

The working mode is considerably changed from the types previously in use. Miguet passes the current through the permanent electrode in which the skin effect is exploited only in the outer layer and from there through the mixed charge composed of different conducting layers to the ground electrode. The charge consists of good conducting lime, coke, or anthracite mixture, and (in cold condition) bad

conducting lime. The current passes through the coke mixture in the direction of the furnace wall and thence spreads round the whole charge between the electrode and furnace wall. Under the electrode collects a clean finished melt of carbide which is tapped at regular moderate intervals, leaving the residual lime roughly distributed around the electrode while at the same time the coal mixture is charged into the furnace. The lime conducts well in the neighbourhood of the high heat of the electrode, as also the coke mixtures occurring near the furnace wall, the combined effect of which is to give a uniform action between the ingredients of the charge throughout the furnace.

The Miguet furnace possesses a circular outline which, for the emplacement of the transformer below the furnace is advantageous, and the arrangement is in fact of profound significance for the whole construction of the furnace. It allows the main cables to be carried near the electro-phase alloys so that the unalloyed leads are very short and consequently the subdivided leads of the furnace. Moreover, the circular section of the furnace permits of a regular distribution of the leads around the furnace and secures a particularly favourable performance in which only 10,000 to 15,000 amperes are required. For details of the furnace see Taussig, "Die Industrie des Kalziumkarbides," Wien, 1930.

The subsequent treatment of the carbide requires special machinery, according to whether the material is to be used for the preparation of acetylene or for the manufacture of cyanamide. In the former case the clean ingots are broken into large blocks and fed into jaw crushers, from whence it is passed for granulation through slow-moving rolls, the object being to attain the desired state of division with a minimum production of dust. The crushed material is sized on drums or rotary screens, which deliver the product in sizes varying from large lumps 8 by 4 in., for the manufacture of acetylene on a large scale, to 16–30 mesh size for automobile lamps, etc. A sheet-iron plant, where steel drums and air-tight cans are manufactured for storing and transport of the carbide, is a necessary part of every works. The standard packages are 100, 110, 200, 220 lb. net weight of carbide, and small tins from 1 to 25 lb. for lamps.

The largest use of calcium carbide is for making acetylene, but the cyanamide (*q.v.*) industry is dependent on calcium carbide for its manufacture. For this purpose it is necessary to reduce the material to a fine state of division and to prevent oxidation and explosion this operation is usually performed in an atmosphere of nitrogen.

The manufacture of calcium carbide at prices prevailing in normal times depends upon the supply of cheap electric power. Norway and Sweden, having abundance of water-power and deposits of suitable limestone, have long been the largest producers of carbide. According to C. Bingham (J.S.C.I. 1918, 37, 85R), the production of a ton of carbide requires 4,250 units of electric power; this figure includes not only the current required for the furnaces themselves but that absorbed by transformers and leads, as also that consumed by motors to drive crushers, elevators, pumps and drum-making plant.

Calcium Cyanamide, $CaCN_2$.—When calcium carbide is heated to 1,100° it decomposes into calcium and carbon, and this elemental decomposition it was thought formed the first stage in the formation of calcium cyanamide (*v. infra*). The calcium forms nitride with nitrogen, which combines with the carbon to give calcium cyanamide (Z. anorg. Chem. 1905, 46, 1358).

The nitrogen required for the production of calcium cyanamide, "nitrolim," from calcium carbide for manurial purposes, is obtained from the air by the Linde Company's plant, which produces both nitrogen and oxygen. The union of powdered calcium carbide and nitrogen takes place with the evolution of heat; hence the temperature has to be maintained between 800° and 1,000°, as at higher temperatures the calcium cyanamide decomposes. The absorption occupies 30 to 40 hours, and the product is a coke-like material which is ground to powder before being placed on the market.

Erhlich (Z. Elektrochem. 1922, 28, 529) shows that decomposition of calcium cyanamide commences above 1,100° and is not determined solely by temperature. Above 1,200° calcium cyanamide sublimes, but at 1,300° a re-formation of calcium carbide can be deduced. Pure calcium cyanamide sublimes at 1,300° without previously melting. The dissociation pressure according to the equation

$$CaC + N_2 \rightleftharpoons CaCN_2$$

at 1,000° is 2·5 mm., at 1,100° is 14 mm., at 1,140° is 32 mm., at 1,190° is 73 mm.

Franck and Bodea (Z. angew. Chem. 1931, 44, 379) find that commercial electrolytic calcium exhibits a maximum in the nitrogen adsorption-temperature curve at about 440°, and a second much higher maximum at 910°, *i.e.* in the neighbourhood of the melting-point; after remelting the metal yields only a sharp maximum at about 460°, and after redistillation only the maximum at 910°. At all temperatures above and below the peaks the adsorption is in all cases practically zero. It is suggested that neither α-Ca nor β-Ca reacts readily with N_2, but that reaction occurs during the transition, for which the optimum temperature is 400°; this view is supported by the observed influence of Na and Li (present in the commercial metal) in increasing the reactivity by virtue of their favouring the opening up of the Ca lattice. The primary reaction between Ca_3N_2, C, and N_2 at 800–1,100°, yields CaC_2, which then reacts with N_2 to form $CaCN_2$; when Ca_3N_2 is heated with C in a vacuum at 900° the pressure at first rises and then falls to its initial value, and the product contains CaC_2 56·9, $CaCN_2$ 31·1, Ca_3N_2 4·3%. The theory that Ca_3N_2 is an intermediate product of the commercial manufacture of $CaCN_2$ from CaC_2 is thus untenable. CaO and HCN react slightly at room temperature, whilst at 350° the product contains 35% $Ca(CN)_2$. Pure $CaCN_2$ may be prepared by heating $Ca(CN)_2$ at 600° in N_2; by heating the

product with **C** at 1,050° in vacuum a white $\mathbf{CaC_2}$ of 95% purity may be prepared, the impurities being only $\mathbf{CaCN_2}$ (2–3%) and **CaO**.

Cochet (Z. angew. Chem 1931, **44**, 367–372), using the compensation balance method and apparatus for the investigation of heterogeneous reactions at high temperature, states that the results are obtained with greater rapidity and are of higher accuracy than those derived from v.-p. measurements. Equilibrium in the system $\mathbf{CaC_2–N_2–C–CaCN_2}$ at temperatures from 1,220° to 1,390° is bivariant The third phase, *i e.* in addition to **C** and **N**, must be a solution of $\mathbf{CaC_2}$ in $\mathbf{CaCN_2}$; this solution is the true reactant and its concentration is a determining factor of the equilibrium. The reaction up to at least 1,325° is completely reversible and is $\mathbf{CaC_2+N_2 \rightleftharpoons CaCN_2+C}$, but at 1,400° the $\mathbf{CaCN_2}$ decomposes with loss of **Ca** and **N** ·

$$\mathbf{CaCN_2+C \rightarrow Ca+N_2+2C},$$

at 1,600° the whole of the **Ca** present as $\mathbf{CaCN_2}$ volatilises. At 1,120°–1,130° $\mathbf{CaCN_2}$ containing 29% **N** is stable, but with rise of temperature to 1,200° the **N** content falls rapidly to about 21%, at higher temperature it falls relatively slowly, and at 1,500° is 17 5%

Calcium Carbonate, $\mathbf{CaCO_3}$, occurs as a major constituent of the earth's crust in beds of limestone, chalk and marble, it also constitutes the principal ingredient in egg shells, mollusc shells and coral. It is formed when the oxide or hydroxide is exposed to moist air containing carbon dioxide, but is not produced by the action of dry carbon dioxide on dry lime It may be obtained in the pure state by dissolving chalk, or marble, or calcined oyster shells in hydrochloric acid, precipitating the alumina, oxide of iron, and earthy phosphates by ammonia or milk of lime, filtering, then precipitating the calcium by ammonium carbonate, washing and drying

Calcium carbonate is dimorphous, crystallising in the hexagonal system as calcite (*q v.*) and in the rhombic system as aragonite (*q v*)

Bragg (Proc Roy Soc. 1924, (A), **105**, 16), by X ray analysis, shows that the crystalline structure of aragonite is based on the simple orthorhombic lattice, the sides of which are 4 94 Å, 7 94 Å, 5 72 Å. The cell contains 4 mols of $\mathbf{CaCO_3}$ and the symmetry is that characterising the space group Q_h^{16}.

When aq $\mathbf{(NH_4)_2CO_3}$ is added to aq. $\mathbf{CaCl_2}$ the formation of rhombic as opposed to acicular crystals of $\mathbf{CaCO_3}$ is favoured by low temperature, low $\mathbf{(NH_3)}$, and high concentration of reactants Below 35° spherulitic crystals appear (T. Noda, J Soc. Chem Ind. Japan, 1934, **37**, 319).

Boeke (Jahrb. Min 1912, **1**, 91) finds that Iceland spar fuses in $\mathbf{CO_2}$ at 1,289°/110 atm. without decomposing. Fusion of mixed $\mathbf{CaCO_3}$–**CaO** forms a eutectic of 91% $\mathbf{CaCO_3}$, 9% **CaO** at 1,218°, but no mixed crystals or intermediate product. The heating curves indicate an inversion of $\mathbf{CaCO_3}$ at 970° from calcite into $\alpha\mathbf{CaCO_3}$.

Calcium carbonate, when heated to full redness in open vessels, is decomposed into carbon dioxide and lime. If the carbonate be ignited in a closed vessel, it fuses and resolidifies to a mass of marble like calcite. According to Becker (Jahrb Min 1886, **1**, Ref. 403), any form of $\mathbf{CaCO_3}$, even at a low pressure, is changed on heating in a closed space with exclusion of air into the rhombohedral form without fusion. The crystalline forms of calcium carbonate dissociate very slowly below 400°, at this temperature the dissociation pressures are of the order of 0 003–0 009 mm. At 425° aragonite is transformed into calcite within an hour when heated in a vacuum. Besides the two well known forms a third crystalline form, referred to as $\mu\mathbf{CaCO_3}$ (Merwin and Williamson, Amer. J. Sci 1909, **41**, 473), is obtained along with calcite and aragonite by precipitation at 60°. It has *d* 2 54, and can be separated from calcite, *d* 2 71, and aragonite, *d* 2 88, by flotation in a liquid *d* 2 6 If small quantities of the precipitated carbonate are thrown into a fused mixture of sodium and potassium chlorides in equivalent proportions, no carbon dioxide is evolved, but the carbonate becomes crystalline calcite, usually in aggregations of crystals like snow crystals (Bourgeois, Bull. Soc chim. 1882, (ii), **37**, 447)

The melting-point of $\mathbf{CaCO_3}$ containing only 0 38% **CaO** is 1,339° at 1,013 atm pressure (Smith and Adams, J Amer Chem. Soc 1923, **45**, 1167).

The solubility of calcite and aragonite in water at 25°, 50°, 100°, determined by the direct method in which large silica flasks were employed, was as follows. calcite 0 01433, 0 01504, 0 01779 g per litre, aragonite 0 01528, 0 01617, 0 01902 g. per litre. In contact with air containing 3 7 $\mathbf{CO_2}$ per 10,000 the solubility of calcite was 0 04608 g per litre at 25°, and 0 02925 at 50° (Kendall, Phil Mag. 1912, (VI), **23**, 958–976).

By treating an aqueous suspension of $\mathbf{CaCO_3}$ with $\mathbf{CO_2}$ under 56 atm. pressure at 18°, Haehnel (J pr Chem. 1924, [ii], **107**, 165) obtained a solution containing 0 393% $\mathbf{CaCO_3}$ corresponding with 0 637% calcium hydrogen carbonate This figure is higher than that found by McCoy *and Smith (J. Amer Chem. Soc. 1911*, **33**, 468) Both prepared calcium carbonate and Iceland spar gave the same result. The solubility of the $\mathbf{CaCO_3}$ depends on the pressure of the $\mathbf{CO_2}$ to which the mixture is subjected It reached the above maximum at 46 atm, not at 16 atm. as stated by McCoy and Smith.

A litre of water dissolves about 18 mg of calcium carbonate. The solution has a slight alkaline reaction. Gothe (Chem.-Ztg. 1915, **39**, 305) gives the solubility of $\mathbf{CaCO_3}$ in water free from $\mathbf{CO_2}$ as being 31 0 mg per litre It is increased by the presence of chlorides, nitrates, and sulphates in the water, but decreased by alkaline carbonates, and by chlorides, nitrates, and sulphates of the alkaline earths. When boiled with water $\mathbf{CaCO_3}$ slowly dissociates with evolution of $\mathbf{CO_2}$ This dissociation stops at a certain point, and is prevented if a solution of $\mathbf{Ca(OH)_2}$ (saturated at the ordinary temperature) is added to the boiling calcium carbonate in water in the proportion of 15 c.c. per litre. Sodium carbonate (0 05 g. per litre) prevents

dissociation (Cavazzi, Gazzetta, 1917, **47**, ii, 49). Seyler and Lloyd (J.C.S. 1917, **111**, 994) find that the ionic solubility product of calcium carbonate is $[Ca]\times[CO_3]=71{\cdot}9\times10^{-10}$, which gives $[Ca]=14{\cdot}6\times10^{-5}$ for a saturated solution $CaCO_3$ in pure water. In this solution the carbonate is hydrolysed to the extent of 66%. Water containing carbonic acid dissolves it much more readily, forming the acid carbonate $CaH_2(CO_3)_2$, which is known only in solution. Solubility at higher pressures in water containing carbonic acid follows the law of Schloesing pretty closely (Engel, Compt. rend. 1885, **101**, 949). The solubility increases under an increase of pressure only up to 3 g. per litre according to Caro. The solubility of calcite in water, determined at different temperatures by bubbling air containing 3·18 parts of CO_2 per 10,000 until saturation occurs, expressed in parts of $CaCO_3$ per million is: at 1°, 82; 21°, 60; 22°, 57;2 3°, 57; 30°, 55 (Wells, J. Washington Acad. Sci. 1915, **5**, 617; *cf.* J. Amer. Chem. Soc. 1915, **37**, 1704). Cavazzi (Gazzetta, 1916, **46**, ii, 122) finds that the maximum quantity of $CaCO_3$, which after prolonged shaking dissolves at 0° in 1 litre of water saturated with CO_2 and maintained so in the presence of the gas at atmospheric pressure is 1·56 g. (2·5272 g. $Ca(HCO_3)_2$); at 15°, 1·1752 $CaCO_3$ (1·9038 $Ca(HCO_3)_2$). A supersaturated solution is obtainable, containing 2·29 g. $CaCO_3$ per litre. This acid carbonate plays a most important part in nature, for whenever water containing carbonic acid comes in contact with carbonate or silicates of calcium, the calcium is gradually converted into this soluble form and is therefore found in almost all natural waters. Hence also the deposits in kettles and boilers; the formation of which may be prevented by the addition of ammonium chloride to the water.

Hydrates of Calcium Carbonates.—The evaporation of natural solutions of the acid carbonate generally results in the deposition of the ordinary carbonate, forming the stalactites and stalagmites of caverns, travertine, and other forms of deposit; but sometimes the solution yields six-sided rhombic prisms of the *pentahydrate*, $CaCO_3,5H_2O$. These crystals are often found in pumps and pipes leading from wells, also adhering to the *confervæ* in ponds. They keep unaltered under water at 20°, but at slightly higher temperatures lose their transparency and water of crystallisation.

Krauss and Schriever (Z. anorg. Chem. 1930, **188**, 259) state that the *hexahydrate* may be prepared by adding 0·1*N*-sodium carbonate slowly to 0·1*N*-calcium chloride both at 0°. The subsequent washing, drying and examination of the compound must be carried out at a low temperature, since it decomposes at 8°. From experiments on the isobaric dehydration of the hexahydrate it is evident that a *monohydrate* also exists, and this compound has been prepared and examined. The monohydrate is very unstable, even when kept under water at 0°, and on decomposition yields calcite. Densities have been determined as follows: hexahydrate, d_4^0 1·77; monohydrate, d_4^{20} 1·99.

Hume (J.C.S. 1925, **127**, 1036) investigated the hydrates of calcium carbonate as follows: A solution of sucrose 25 g. in 100 c.c. of water was shaken with lime and filtered, the filtrate being treated with carbon dioxide. After two or three days crystals of calcium carbonate hexahydrate were deposited, d^{15} 1·789. In contact with water or above 0° the hexahydrate slowly changes into anhydrous calcium carbonate, but in the sugar-lime mixture it is stable below 10·4° and the anhydrous salt above 17°. Between 10·4° and 17° the stable phase is pentahydrate, d^{15} 1·834. Between 10·4° and 25° the hexahydrate is first precipitated from the sugar solution and then changes slowly into the form most stable at the particular temperature.

Basic Carbonates of Lime.—Calcium oxide commences to adsorb carbon dioxide at a temperature of 415°, forming a basic carbonate of the composition $2CaO{\cdot}CO_2$ (Birnbaum and Mahu, Ber. 1879, **12**, 1547).

Raoult (Compt. rend. 1881, **92**, 1457) shows that when freshly burnt lime is heated in a current of carbon dioxide it glows strongly, forming $2CaO{\cdot}CO_2$, which does not disintegrate in moist air, and does not take up water from steam at 200°. When finely powdered and treated with a little water, it hardens like hydraulic cement. The hydrated product has the composition $CaCO_3{\cdot}Ca(OH)_2$. On heating to dull redness, it loses water and is converted into a mixture of $CaCO_3$ and CaO.

When burnt lime is heated in contact with carbon dioxide for several days, the basic salt, $2CaCO_3{\cdot}CaO$, is obtained, which adsorbs more CO_2, forming a third salt $3CaCO_3{\cdot}CaO$. The carbon dioxide continues to be adsorbed, however, and appears eventually to form the normal carbonate.

Calcium Nitride, Ca_3N_2, is best obtained by passing dry nitrogen over metallic calcium contained in a metal boat and tube heated to bright redness. Two to three hours are required, and the resulting material is fritted and possesses a brownish-red colour. Its fusion point is about 1,200°, sp.gr. 2·63 at 17°. When thrown into water it produces a lively effervescence, yielding ammonia and calcium hydroxide:

$$Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$$

(Moissan, Ann. Chim. Phys. 1903, [vii], **18**, 289). The nitride heated in a current of hydrogen gives a compound having the formula $Ca_3N_2H_4$ (Dafert and Miklauz, Monatsh. 1913, **34**, 1685).

Antropoff and Falk (Z. anorg. Chem. 1930, **187**, 405) investigated the system calcium–calcium nitride by the determination of cooling curves in an atmosphere of argon. The eutectic mixture corresponds with 3–4% of nitride, but the cooling curve shows halts at 780° and 809°. The melting-point of calcium nitride is 1,195°±1°. The heat of formation of calcium nitride obtained by Guntz is 113,250 g.-cal.; Frank and Bodea obtained 102·6±1° kg.-cal. by direct formation of Ca_3N_2 (95–98·2%) in a bomb calorimeter.

By heating the amide in a high vacuum the pernitride Ca_3N_4 has been obtained as a reddish-brown powder, probably mixed with the corresponding imide. It dissolves slowly in H_2O or dilute HCl with formation of NH_3 and N_2. The X-ray spectra contain, besides the imide lines, new lines which cannot be measured owing to a cloudiness which is apparently always found when the pernitride is present. Ba_3N_4 is probably similarly formed (H. Hartmann, H. J. Fröhlich, and F. Ebert, Z. anorg Chem. 1934, 218, 181)

Calcium Azide, $Ca(N_3)_2$, may be obtained by treating calcium hydroxide solution with the aqueous acid or by warming ammonium azide *with excess of calcium hydroxide. The excess* of $Ca(OH)_2$ is precipitated with carbon dioxide and the filtered solution concentrated. Calcium azide forms colourless rhombic prisms (Curtius and Rissom, J. pr Chem. 1898, (ii), 58, 261), is not affected by hammering, but explodes on throwing on to a heated metal plate or *by heating to 144°–156°. The dihydrazinate*, $Ca(N_3)_2,2N_2H_4$, may be prepared by crystallisation of $Ca(N_3)_2$ from anhydrous hydrazine.

Calcium Ammonium, $Ca(NH_3)_6$, is formed when a current of dry ammonia gas is passed over metallic calcium, maintained at a temperature of 15° to 20°. It possesses a brownish red colour, and takes fire when exposed to air (Biltz *and Hüttig, Z anorg. Chem 1920, 114, 241)*

Botolfsen (Ann Chim. 1922, [ix], 18, 5) shows that its formation may take place at −15° to +30° (*cf.* Moissan), at the higher temperature, pressure is required, and if the calcium employed contains sodium as impurity, the product is pasty rather than crystalline. On being heated at about 34° under reduced pressure the substance decomposes explosively, the temperature at which this occurs depends on the pressure

Calcium Amide, $Ca(NH_2)_2$.—Calcium ammonium slowly decomposes forming transparent crystals of calcium amide, hydrogen and ammonia being evolved.

Guntz and Benoit (Ann. Chim 1923, [ix], 20, 5) state that while the amides and imides of barium are obtained by the direct action of the metal on ammonia, those of calcium and strontium are only obtainable indirectly and with some difficulty by decomposition of the corresponding metallic ammonium (*see also* Kraus and Hurd, J. Amer. Chem. Soc. 1923, 45, 2559)

Calcium Imide, $CaNH$, is formed by passing equal volumes of hydrogen and nitrogen over heated calcium. It has not been obtained pure (Dafert and Miklauz, *l.c.*).

By heating the alkaline-earth amides, *$M(NH_2)_2$, at approx. 400°, without removing* the gases formed, the imides MNH are obtained as yellow, cubic, face-centred crystals. X ray data are given (Hartmann, Fröhlich, and Ebert, *l c.*).

Calcium Nitrite, $Ca(NO_2)_2,H_2O$, is prepared by decomposing a boiling solution of silver nitrite with lime water, treating the filtrate with sulphuretted hydrogen and carbon dioxide to remove the silver and excess of calcium, and evaporating at a gentle heat. It crystallises in deliquescent prisms insoluble in alcohol.

Calcium Nitrate.—The hydrate,

$$Ca(NO_3)_2,4H_2O,$$

m.p. 42·4° (Pickering), 42·7° (Richards), 42 89°± 0 03° (d'Ans and Siegler), occurs as a silky efflorescence in limestone caverns, especially those of Kentucky, also on the walls of places where there is much organic refuse. It is found in many well waters, being derived from the soil. It is extremely deliquescent and soluble, and causes rapid disintegration of mortar, and hence is called "saltpetre rot." It may be prepared by dissolving the carbonate in nitric acid, on slow evaporation of the solution the hydrated salt is deposited in monoclinic six *sided prisms terminated by acute pyramids*. With alcohol it forms the compound

$$Ca(NO_3)_2,2C_2H_5OH$$

(d'Ans and Siegler, Z. physikal Chem. 1913, 82, 41). The hydrate is also soluble in alcohol. On evaporating the aqueous solution to dryness *the anhydrous salt of sp gr. 2·472 is obtained*, possessing a warm, bitter taste and readily soluble in water and alcohol. On heating, more strongly, it becomes phosphorescent, as noticed by Baldwin in 1674, and hence is termed *Baldwin's phosphorus*. At a higher temperature, oxygen and nitric peroxide are evolved and with combustible bodies detonation occurs.

The melting-point of $Ca(NO_3)_2$ is 561° (Carnelly). The eutectic point for the system $Ca(NO_3)_2–KNO_3–NaNO_3$ is 175°. The compound $Ca(NO_3)_2,4CO(NH_2)_2$ is formed when $Ca(NO_3)_2$ and carbamide are mixed together with a small quantity of water and dried, or when a suitable proportion of carbamide is added to a melt of the hydrated nitrate. The double compound is easily soluble in water (U S P 1369383, Bosch).

Nitrogen peroxide reacts with calcium oxide at all temperatures up to 400°, giving primarily calcium nitrite and nitrate. Secondary reactions occur at higher temperatures. Above 230° calcium nitrite decomposes:

$$Ca(NO_2)_2=CaO+NO+NO_2;$$

and in the presence of nitrogen peroxide undergoes oxidation at lower temperatures in the following ways:

$$Ca(NO_2)_2+2NO_2=Ca(NO_3)_2+2NO,$$

$$Ca(NO_2)_2+NO_2\rightarrow Ca(NO_3)_2+0\ 5N_2 \text{ at } 450°.$$

The molecular proportions in which the products of decomposition are formed is represented by the equation

$$12\ 02\ Ca(NO_2)_2\rightarrow$$
$$7{\cdot}68\ CaO+4\ 34\ Ca(NO_3)_2+14\ 40\ NO+N,$$

nitrogen and nitric oxide alone being evolved. Above 480° nitrogen peroxide is in addition given off, and at 495° calcium nitrate begins to decompose. Calcium nitrite is not oxidised by oxygen below its decomposition point except in the presence of nitrogen peroxide. The existence of the compound $Ca(NO_2)_2,4H_2O$ was confirmed (Partington and Williams, J.C.S. 1924, 125, 947).

The action of liquid and gaseous nitrogen peroxide at temperatures between 15° and 400°,

and for periods between 5 and 624 hours on calcium carbonate and oxide, and that of nitric oxide on these substances at 400°, have been studied by Briner, Lugrin, and Monnier (Helv. Chim. Acta, 1930, **13**, 64–75). Both in the liquid and gaseous state dry nitrogen peroxide reacts with calcium carbonate according to the equation

$$CaCO_3+3NO_2 \\ =Ca(NO_3)_2+CO_2+NO+27 \text{ kg.-cal.}$$

The amount of nitrogen peroxide adsorbed is proportional to the time of contact, and the rate of adsorption increases rapidly with rise of temperature. With lime both nitrate and nitrite are formed with the liberation of nitric oxide, but the adsorption is irregular by reason of the pasty nature of the product. At 400° nitric oxide does not react with calcium carbonate and is decomposed only to a very slight extent by lime. Under conditions in which the solid may be stirred, nitrogen peroxide in 10% concentration in air is better adsorbed by calcium carbonate than by lime. The use of calcium carbonate in the recovery of nitrous gases is suggested.

The hydrate of calcium nitrate is extensively prepared on the Continent for the manufacture of nitre by mixing vegetable and animal refuse with chalk, marl, cinders, etc., moistening from time to time with liquid stable manure, and exposing to the air for two or three years, when the mass is lixiviated and the crude nitrate of calcium decomposed by carbonate, sulphate, or chloride of potassium. Large quantities of calcium nitrate are now produced by the Haber process.

Calcium Phosphide, Ca_3P_2.—Moissan (Compt. rend. 1899, **128**, 787) obtained calcium phosphide as an amorphous product from pure crystallised calcium and red phosphorus. The two bodies were placed apart in a tube which was exhausted and the phosphorus was gently heated. The vapours evolved combined with the calcium with incandescence. He also obtained it in a brownish-red crystalline form by reduction of pure calcium phosphate with carbon in an electric furnace, using 310 parts and 96 parts respectively of the ingredients and a current of 950 amperes and 45 volts. It melts with difficulty except in the electric furnace, and has a sp. gr. 2·51 at 15°. The crystalline phosphide is decomposed slowly by cold water liberating hydrogen phosphide which is not spontaneously inflammable.

An impure calcium phosphide which is decomposed by water evolving the spontaneously inflammable mixture of liquid and gaseous hydrogen phosphides is utilised for the production of signal fires at sea. The manufacture is carried out in large crucibles divided by a false perforated bottom into two compartments, in the upper of which the pieces of lime are raised to a red heat, the phosphorus placed in the lower compartment being afterwards volatilised by the heat radiated from above. In about 6 hours a charge, yielding 20 lb. of product, is finished. The brown stony mass is immediately worked up into the "lights." These consist of cylindrical tinned-iron boxes, the lower half of which is filled with about 6 oz. of the fragments of phosphide. Two small circular portions of the upper and under surfaces of metal are formed of soft lead, so that they may be pierced by a knife just before being thrown overboard. The tins are supported by a wooden float when in use. The water enters below and the gas issues from the upper outlet, burning with a flame 9 to 18 in. high, lasting about half an hour. Larger but similar "lights" are prepared to be placed in a bucket of water on deck.

Calcium Phosphite, $CaHPO_3,H_2O$, separates as a crystalline crust from a solution of the ammonium salt mixed with calcium chloride. It is sparingly soluble in cold water, and the solution decomposes when heated depositing a basic salt. It gives off its water at 100°. It is a white crystalline powder, which, on heating, evolves spontaneously inflammable phosphoretted hydrogen, accompanied by slight detonations. At a higher temperature it becomes incandescent, and leaves a residue of calcium phosphate.

An *acid phosphite*, $CaH_4(PO_3)_2,H_2O$, is obtained as a crystalline crust by acting upon marble with aqueous phosphorous acid as long as carbon dioxide escapes. The crust consists of needle-shaped crystals soluble in water, and losing their water at 100°.

Calcium Hypophosphite,

$$Ca(PO_2H_2)_2 \text{ or } CaH_4(PO_2)_2,$$

is prepared by boiling phosphorus with milk of lime :

$$3Ca(OH)_2+2P_4+6H_2O \\ =2PH_3+3CaH_4(PO_2)_2$$

On evaporation the hypophosphite is obtained in monoclinic flexible prisms insoluble in alcohol. When heated it evolves phosphoretted hydrogen and water, leaving calcium pyrophosphate. It has therapeutic properties.

Monocalcium Phosphate, $CaH_4(PO_4)_2$. Bassett (Z. anorg. Chem. 1907, **53**, 55) obtained the anhydrous salt in long shining prisms by digesting $CaCO_3$ with concentrated H_3PO_4 in an air bath for 6½ hours followed by filtration on a Bucknell funnel washing with acetone and ether.

The monohydrate is obtained in rhombic tables by dissolving the monophosphate in phosphoric acid and allowing the solution to evaporate spontaneously. It has a strong acid reaction, deliquesces in air, dissolves readily in water with decomposition, and crystallises in triclinic pinacoidal prisms (Groth, "Chemische Krystallographie," II, p. 830; Leipzig, 1908).

The hydrate fuses on heating, giving up its water, and at 200° it parts with the elements of water, leaving a mixture of calcium pyrophosphate and metaphosphoric acid :

$$2CaH_4(PO_4)_2=Ca_2P_2O_7+2HPO_3+3H_2O$$

When the mixture is heated to a still higher temperature, pure calcium metaphosphate remains (Spring, Bull. Soc. chim. Belg. 1907, **21**, 91).

Superphosphate of Lime is a mixture of monocalcium phosphate and calcium sulphate, which is manufactured as a manure. It is prepared by acting on bone-ash, rock phosphate,

phosphorites, or other mineral phosphates with two thirds weight of sulphuric acid:

$$Ca_3(PO_4)_2+2H_2SO_4 = CaH_4(PO_4)_2+2CaSO_4$$

Besides its use as a manure for root crops it is used also in the manufacture of phosphorus.

On dissolving increasing quantities of monocalcium phosphate in a given weight of water at a constant temperature the amount of free phosphoric acid continually increases, and tends towards a limit in accordance with the equation

$$2CaH_4(PO_4)_2 \rightleftharpoons CaH_4(PO_4)_2+CaHPO_4+H_3PO_4$$

In superphosphate the dicalcium phosphate is seldom present unless excess of acid has been used. Aita considers that reaction does not take place according to Kolbe's view, in two stages, but is more correctly represented by the equation.

$$5Ca_3(PO_4)_2+11H_2SO_4 = 4CaH_4(PO_4)_2+2H_3PO_4+11CaSO_4.$$

With rise of temperature there is found free phosphoric acid and dicalcium phosphate which gradually interact to form the monocalcium phosphate (Annali Chem. Appl. 1918, 10, 95).

Monocalcium phosphate is used as a basis of organophosphors (E. Tiede and H Chomse, Ber. 1935, 68, [B], 146) Weighed quantities of $Ca(H_2PO_4)_2,H_2O$ and the organic compound are intimately mixed in a porcelain mortar and heated at about 250° on Pt foil or porcelain until the mass has become plastic The phosphate is thereby converted into a mixture of $Ca(PO_3)_2$ and $Ca_2P_2O_7$ Luminous preparations are obtained with uranin, phenanthraquinone, and the three carboxylic acids:—

$$m\ C_6H_4(CO_2H)_2,\quad C_6H_3(CO_2H)_3,\quad C_6H_2(CO_2H)_4;$$

poor results with 1-hydroxynaphthoic acid, and negative results with salicylic acid and anthracene. Small amounts of metals (Cu, Bi, Mn) do not induce luminescence

Dicalcium Orthophosphate, $Ca_2H_2(PO_4)_2$ — An aqueous solution of phosphoric acid acts on precipitated chalk, forming small needle shaped crystals of dicalcium phosphate. Dried at 100°, the salt contains $5H_2O$, which it does not lose below 115°. It is soluble in ammonium citrate, and in boiling aqueous solution it is partially decomposed into tricalcium phosphate.

On mixing boiling solutions of sodium phosphate, calcium chloride, and acetic acid, $Ca_2H_2(PO_4)_2,H_2O$ is formed; if the solutions are mixed in the cold, $Ca_2H_2(PO_4)_2.5H_2O$ is the product (Millot, Bull. Soc. chim. 1880, [ii], 33, 194). The pentahydrate is also formed (Joly and Sorel, Compt. rend. 1894, 118, 741) when cold saturated solutions of sodium phosphate and calcium chloride are mixed in the presence of hydrochloric acid.

When solutions of calcium chloride and ordinary sodium phosphate are mixed, a white crystalline precipitate of $Ca_2H_2(PO_4)_2.4H_2O$ is thrown down. It is this salt which is occasionally deposited from wine in stellar aggregates According to Becquerel and Berzelius, a trihydrate may also be obtained

Calcium Orthophosphate, $Ca_3(PO_4)_2$, occurs pure in the mineral osteolite, and as $Ca_3(PO_4)_2,2H_2O$ in ornithite. Combined with calcium fluoride or chloride, it occurs in nature as apatite (*q v.*). Apatite is phosphorescent when heated, especially after exposure to radium

Calcium phosphate also forms a principal constituent of the coprolites frequently found in extensive beds in the stratified rocks, and this forms the chief source of the rock phosphate of commerce. It forms about 80% of the inorganic material of bones.

It is obtained in the amorphous state by precipitating an ammoniacal solution of calcium chloride with excess of hydrogen disodium phosphate. The precipitate is gelatinous, but dries to a white earthy powder, nearly insoluble in water, but decomposed by long boiling into an insoluble basic salt of the composition, $Ca_3(PO_4)_2 \cdot Ca_2(PO_4)OH$, and a soluble acid salt This reaction also occurs slowly in the cold Calcium phosphate is also soluble in water containing carbonic acid (1 part in 1,789 parts of water saturated with carbon dioxide), ammonium salts, sodium nitrate, sodium chloride, and other salts Its adsorption by the roots of plants is therefore promoted by the agency of saline solutions.

Bassett (J C S. 1917, 111, 620) has shown that only two phosphates more basic than dicalcium phosphate exist these are tricalcium phosphate, $Ca_3P_2O_8$, and hydroxy apatite,

$$(Ca_3P_2O_8)_3,Ca(OH)_2.$$

The latter is the only stable solid phase over a range of acidity of great practical importance, as it can exist in faintly acid, neutral, or alkaline solutions. It is probable that this compound is the only calcium phosphate that can permanently exist under normal soil conditions. Bone phosphate is considered to be a mixture of hydroxyapatite and calcium carbonate, with small amounts of adsorbed bicarbonates of sodium, potassium, and magnesium.

Danneel and Fröhlich (Z. anorg Chem. 1930, 188, 14) suggest that the wide variation of the figures given in the literature for the solubility of tricalcium phosphate in water is largely due to the fact that a substance having the composition $Ca_3P_2O_8$ has hitherto seldom been obtained. Specimens in which the ratio Ca . P varied between 2 99 and 3 01 have been prepared by precipitating solutions of monocalcium phosphate with dilute ammonia, and the result of shaking these with water has been investigated. Equilibrium is established in less than 8 hours. Warington's statement that the composition of the solution is a function of the relative amounts of solid and water has been confirmed. Calcium and phosphoric acid are not necessarily present in the solution in stoichiometric proportions. With very little water the CaO/P_2O_5 ratio is 1 : 1; with 5 litres per g of solid it is 2 : 1; and with 10 litres per g 2 53 1, which last named ratio is not changed by further dilution. It is considered probable that water decomposes tricalcium phosphate into

tetracalcium phosphate, a salt $Ca_5H_2(P_2O_8)_2$, and monocalcium phosphate, and that these form a solid solution.

Calcium orthophosphate may be obtained in the crystalline form by heating dicalcium pyrophosphate with water, whereby it is resolved into phosphoric acid and tricalcium phosphate, which separates in rectangular plates:

$$3Ca_2P_2O_7+3H_2O=2Ca_3(PO_4)_2+2H_3PO_4$$

Tricalcium phosphate is not decomposed by ignition. It is not reduced by CO, but H reduces it at 1,300° to a mixture of CaO and phosphorus. Carbon begins to reduce it at 1,400°. It is not decomposed by silica in an inert atmosphere, but chemical combination occurs at 1,150°, and the product is completely reducible by carbon. The compound has the composition $3CaO,3SiO_2,P_2O_5$, and is indicated by a strong maximum on the freezing-point curve of the system calcium phosphate–calcium silicate.

Briner and Monnier (Helv. Chim. Acta, 1930, **13**, 80) show that no reaction occurs between calcium phosphate and sulphur dioxide at the ordinary temperature, but at higher temperatures a reaction, represented by the equation

$$2Ca_3(PO_4)_2+3SO_2 = 2CaSO_4+2Ca_2P_2O_7+S$$

occurs.

Thilo (Z. physikal. Chem. 1930, **148**, 361) states that when a suspension of calcium phosphate is dissolved in sulphurous acid the following equilibrium is set up:

$$Ca(H_2PO_4)_2+nCa(HSO_3)_2 \rightleftharpoons 2CaHPO_4+(n+1)SO_2+(n-1)CaSO_3 +(n+1)H_2O,$$

in which n depends on the ratio CaO/P_2O_5 in the original suspension. By removing the sulphur dioxide with a current of nitrogen at the ordinary temperature a precipitate consisting of dicalcium phosphate and calcium sulphite is obtained. Contrary to the findings of Mebane, Dobbins, and Cameron (J. physical Chem. 1929, **33**, 961), the phosphoric acid is always present as the dicalcium salt, whatever be the initial ratio of acid to lime. The proportion of calcium sulphite to dicalcium phosphate depends on the ratio CaO/P_2O_5 in the suspension, as much calcium as possible being precipitated as phosphate and the remainder as normal sulphite. The composition of the precipitate is independent of the duration of the experiment, the velocity of the nitrogen stream or the concentration of the solution. The rate of evolution of sulphur dioxide decreases rapidly to a minimum, and the formation of the precipitate begins immediately before this minimum is reached. Afterwards, the rate of evolution increases to a maximum and then slowly decreases, indicating that the reaction is autocatalytically accelerated by the precipitate.

Briner and Lugrin (Helv. Chim. Acta, 1930, **13**, 76) find that neither liquid nor gaseous nitrogen peroxide has appreciable action on dry calcium phosphate, even with periods of contact of 35 days. In the presence of traces of water the action is represented by

$$3NO_2+Ca_3(PO_4)_2+H_2O = Ca(NO_3)_2+2CaHPO_4+NO,$$

and, with greater amounts of water, by

$$6NO_2+Ca_3(PO_4)_2+2H_2O = CaH_4(PO_4)_2+2Ca(NO_3)_2+2NO.$$

No nitrite is formed in either case, any nitrous acid formed either decomposing to give nitric acid, $3HNO_2=HNO_3+H_2O+2NO$, or being oxidised by the nitrogen peroxide,

$$HNO_2+NO_2=HNO_3+NO.$$

Colloidal calcium phosphate may be prepared by adding slowly with continuous shaking a hot normal solution of sodium phosphate to an equal volume of normal solution of $CaCl_2$ containing a definite amount of protective colloid such as gum arabic or gelatin (de Toni, Kolloid-Z. 1921, **28**, 145).

Colloidal calcium phosphate with calcium carbonate has been prepared by mixing sodium phosphate, sodium carbonate and calcium chloride solutions in aqueous gelatin solution at 95°. The ratio of the two salts can vary greatly (Stella, Kolloid-Z. 1927, **43**, 21).

Dieckman and Houdremont (Z. anorg. Chem. 1921, **120**, 129) give the melting-point of tricalcium phosphate as 1,670°. Oxyapatite, $3(Ca_3P_2O_8),CaO$, m.p. 1,540°, *d* 2·99, is formed by heating tricalcium phosphate with calcium carbonate, the formation being complete at about 1,450°. By melting oxyapatite with calcium pyrophosphate a very soluble tricalcium phosphate is obtained. The solubility of tricalcium phosphate in 2% citric acid was found to be affected by the temperature to which it was heated. Starting at 94·6% it fell to 60% at 540°, and then rose steadily to 96·2% at the melting-point. Oxyapatite has a solubility of 55% in citric acid.

M. A. Bredig, H. H. Franck, and H. Füldner (Z. Elektrochem. 1933, 39, 959–969; *cf.* 1932, A. 469) have prepared mixed apatites containing the following bivalent groups in place of F: Al_2O_4, Fe_2O_4, and $CaCN_2$. Carbonate-mixed-apatite has been characterised by its X-radiogram, and most naturally occurring Ca phosphates consist of it. The materials of bones and teeth are hydroxyoxyapatites. The transformation of the two forms of $Ca_3P_2O_8$ is very sensitive to CaO and H_2O, and this is explained on the basis of stability of hydroxyoxyapatites.

Tetracalcium Phosphate.—Phosphorus in basic slag is present as tetracalcium phosphate, $4CaO,P_2O_5$; less basic phosphates are reduced by molten iron, forming iron phosphide, Fe_3P (La Metallurgia, 1912, 9, 28). $4CaO,P_2O_5$, m.p. 1,630°, has a high solubility in citric acid, but if heated for some time at 1,000° it falls to 25%.

Calcium Pyrophosphate, $Ca_2P_2O_7$, is prepared by the action of aqueous pyrophosphoric acid upon lime water, or sodium pyrophosphate upon calcium chloride. If the precipitate thus obtained is dissolved in sulphurous acid and the solution heated, the salt separates as a crystalline crust. The crystals contain four molecules of water.

Calcium Metaphosphates.—The monosalt $Ca(PO_3)_2$ is obtained by dissolving calcium carbonate in orthophosphoric acid, evaporating, and heating the residue to 316°. It is an insoluble white powder

The dimetaphosphate $Ca_2(PO_3)_4,4H_2O$ is obtained pure in the crystalline form by precipitating the corresponding alkali salt with excess of calcium chloride It is insoluble in water, but is decomposed by strong sulphuric acid. A double dimetaphosphate of calcium and ammonium,

$$Ca(NH_4)_2(PO_3)_4,2H_2O,$$

is obtained in spicular crystals by mixing a solution of calcium chloride with excess of the ammonium salt. It is insoluble in water

Phosphato-chlorides of Calcium are obtained by evaporating solutions of tricalcium phosphate in hydrochloric acid A saturated solution, on spontaneous evaporation, deposits rhomboidal plates of

$$7CaH_4(PO_4)_2\cdot CaCl_2,14H_2O$$

If the solution is evaporated on the water bath, dicalcium phosphate is first deposited, then, on further evaporation, the above phosphatic chloride comes down, and afterwards white scales of $CaH_4(PO_4)_2\ CaCl_2,H_2O$ When a solution of dicalcium orthophosphate in hydrochloric acid is saturated at ordinary temperatures with tricalcium phosphate, then mixed with half the quantity of hydrochloric acid already contained in it, and evaporated, on cooling below 6° crystals separate having the composition $4CaH_4(PO_4)_2\ CaCl_2,8H_2O$ (Erlenmeyer, Jahresber 1857, 146)

Calcium Silico-Phosphate.—According to Carnot and Richard (Compt rend 1883, 97, 316) the brownish black slag, formed in working the Thomas Gilchrist process at Joeuf (Meurthe-et-Moselle), is covered with black crystals, some of which are slender needles, others right rhombic prisms with brilliant faces, frequently aggregated in columnar masses terminating in vitreous, translucent, blue crystals Similar blue crystals are found in the cavities, possessing the constant composition

$$8P_2O_5\ 8SiO_2\ Al_2O_3\ FeO\ 36CaO,$$

essentially a calcium silico phosphate,

$$Ca_3(PO_4)_2+Ca_2SiO_4.$$

Calcium Arsenates.—Dicalcium arsenate occurs native as *haidingerite*,

$$Ca_2H_2(AsO_4)_2,H_2O,$$

and *pharmacolite*,

$$Ca_2H_2(AsO_4)_2,5H_2O,$$

and may be prepared by adding a solution of disodium arsenate to excess of calcium chloride The tetrahydric arsenate obtained by addition of lime water to arsenic acid is soluble, while the tricalcium arsenate is insoluble in water, and may be prepared by precipitating calcium chloride with trisodium arsenate. On evaporating a hydrochloric acid solution of calcium ammonium arsenate with platinum chloride, the mass left on ignition of the platinochloride is found to contain fine white prisms of the tri calcium orthoarsenate, $Ca_3(AsO_4)_2$, insoluble in acids. The meta arsenate, $Ca(AsO_3)_2$, is formed as an insoluble crystalline powder when mixtures of arsenious anhydride and calcium carbonate are ignited.

According to R. H. Robinson (J. Agric. Res. 1918, 13, 281), pure calcium hydrogen arsenate ($CaHAsO_4,H_2O$) may be prepared by pouring an acidified solution of calcium chloride into an acidified solution of sodium hydrogen arsenate It forms a heavy voluminous precipitate which may be obtained crystalline. It becomes anhydrous at 175°. Tricalcium arsenate,

$$Ca_3(AsO_4)_2,2H_2O,$$

may be prepared by pouring an alkaline calcium chloride solution into an alkaline sodium hydrogen arsenate solution, when a heavy, voluminous, sparingly soluble precipitate of sp gr 3 23 is formed

Basic Calcium Arsenate.—Hydrolysis of tri calcium arsenate or calcium ammonium arsenate yields a basic calcium arsenate,

$$3Ca_3(AsO_4)_2,Ca(OH)_2,$$

0 00488 part of which dissolves in 100 parts of water at 25°. It is analogous to hydroxyapatite, and, like the latter, retains the water tenaciously (H. V Tartar, L Wood, and E Hiner, J Amer. Chem Soc 1924, 46, 809).

Calcium arsenate appears to be now generally prepared by heating a mixture of milk of lime and arsenious oxide (white arsenic) into which chlorine is passed, whereby an insoluble arsenate is produced together with a soluble chloride (H P. Basset and E. C. Lathrop, U S P. 1590043, 20/12/21, issued 23/6/26)

The toxicity of calcium arsenates as insecticides decreases with the increase of the molecular ratio

$$CaO:As_2O_5,$$

but is not greatly affected by $Ca(OH)_2$ in the presence of $Ca_3(AsO_4)_2,H_2O$. The basic calcium arsenates have a constant toxicity which is lower than that of the acid calcium arsenate (Hendricks, Bacot and Young, Ind. Eng Chem 1926, 18, 50)

Calcium Ammonium Arsenate,

$$Ca(NH_4)AsO_4,7H_2O,$$

is produced by mixing a hot solution of arsenic acid in excess of ammonia with calcium nitrate or chloride; tabular crystals are deposited on cooling. In a vacuum over sulphuric acid they become $Ca_2(NH_4)H_2(AsO_4)_3,3H_2O$, and when dried at 100° have the composition

$$Ca_6(NH_4)H_5(AsO_4)_6,3H_2O.$$

On ignition they are converted into calcium pyroarsenate, $Ca_2As_2O_7$ (Bloxam, Chem. News, 1886, 54, 168).

Another salt, $Ca(NH_4)_2H_2(AsO_4)_2$, is precipitated by adding excess of ammonia to a solution of dicalcium arsenate in nitric acid, the flocculent precipitate soon becoming a mass of needles The same salt is obtained in crystals belonging to the regular system when the solution of the dicalcium salt is only partially precipitated and allowed to stand; hence it appears to be dimorphous (Baumann, Arch Chem. 1844, 39, 10)

Calcium Chloroarsenate.—C. M. Smith (J. Washington Acad. Sci. 1935, **25**, 435) has prepared the compound $(CaCl)_2HAsO_4,2H_2O$ by addition of $CaHAsO_4,H_2O$ to a solution of $CaCl_2$ in water.

Calcium Meta-arsenite. — Krestovnikov and Lyutringshauzen (Min. Ssyrje, 1930, **5**, 870; Chem. Zentr. 1931, i, 1257) find that the interaction of As_2O_3, finely divided $Ca(OH)_2$, and H_2O is effected at 100° with vigorous stirring. The product is amorphous; solubility in H_2O at 15°, 0·04–0·05%.

Calcium Silicide, $CaSi_2$, corresponds with the carbide CaC_2. Pure disilicide, $CaSi_2$, is prepared by heating the monosilicide at 1,000°–1,010° in a current of hydrogen. If excess of Si is present this unites with the hydride present to form a further quantity of disilicide. The silicide dissolves in HCl with formation of yellow silicone without production of spontaneously inflammable silicon hydride (Wöhler and Müller, Z. anorg. Chem. 1921, **120**, 49–70).

Dodero (Compt. rend. 1934, **198**, 1593), by *electrolysis of a molten* $CaSiO_3$ *bath*

$$(SiO_2+CaCO_3+2CaF_2+\tfrac{1}{3}CaCl_2),$$

at 25 amperes per sq. cm., obtained cathodic mixtures of $CaSi_2$ and Si in proportions depending on the temperature. $CaSi_2$ was practically the sole product at the m.p. of the bath, 1,000°. Yield about 2·5 g. per hour.

Calcium Monosilicide, CaSi or Ca_2Si_2.—The compound is formed free from disilicide when a mixture of calcium and silicon in atomic proportion or with excess of silicon up to 100% is heated in a magnesia boat in an atmosphere of carbon dioxide at a temperature of 1,050°. After a quarter of a minute a violent reaction takes place and the mass becomes incandescent. It must then be cooled rapidly. The mass breaks up readily into small lustrous metallic leaflets and larger crystals. The density of the substance containing a small amount of unconverted silicon is 2·346. By dilute acids it is attacked readily with the evolution of a spontaneously inflammable gas which is probably silicon hydride (silicon-ethylene) and ignites yielding hydrated silica,

$$CaSi{:}SiCa+4HCl=2CaCl_2+H_2Si{:}SiH_2$$

(Wöhler and Müller, *l.c.*).

Crucibles made of talc and alumina in the ratio 5 : 2 are not attacked by calcium silicides (Wöhler and Schliephake, Z. anorg. Chem. 1926, **151**, 1). The calcium in small pieces was put into the heated crucible and prepared silicon powder added. Thermal analysis showed the formation of a compound $CaSi_2$ (41·6% Ca), m.p. 1,020°. The presence of the monosilicide CaSi, m.p. 1,220° was also confirmed. Indications of a third silicide, Ca_2Si, m.p. 920°, were obtained.

Tamaru (Z. anorg. Chem. 1909, **62**, 81) found that molten silicon is miscible with molten calcium in all proportions.

Kolb (Z. anorg. Chem. 1909, **64**, 342), by heating together calcium and silicon, obtained two silicides according to the component in excess. The products contain 53·5% and 36·68% silicon respectively, corresponding approximately with the formulæ Ca_6Si_{10} and $Ca_{11}Si_{10}$. Both silicides are crystalline, evolve hydrogen with acetic acid, and evolve spontaneously inflammable silicon hydride with dilute hydrochloric acid. Silicones are obtained with strong hydrochloric acid. Both silicides absorb nitrogen near 1,000°, the products having the respective compositions $CaSi_2N_3$ and $Ca_{11}Si_{10}N_{10}$.

Technical Preparation of Calcium-Silicon Alloys.—R. Weiner (Z. Elektrochem. 1934, **40**, 624) has prepared a Ca–Si alloy (approx. 30%) by heating CaC_2, SiO_2, and C in a 20-kw. electric furnace, using mainly resistance heating. The alloy, as formed, should be removed from the hottest zone, in which it is unstable. A similar product is formed from CaO, SiO_2, and C.

Calcium Silicates.—Calcium oxide is an important base in a large number of natural silicates, and is the principal basic constituent of the following minerals: wollastonite, $CaSiO_3$, or tabular spar, occurring in monoclinic crystals; okenite, $CaH_2(SiO_3)_2,2H_2O$; zonalite, $4CaSiO_3,H_2O$; gyrolite, $Ca_2H_2(SiO_3)_3,H_2O$; and apophyllite, $H_7KCa_4(SiO_3)_8+4{\cdot}5H_2O$.

Gorgeu (Compt. rend. 1884, **99**, 256) obtained artificial wollastonite by fusing 1 g. of silica with 15 g. calcium chloride and 3 g. common salt at a cherry-red heat in a current of moist air for half an hour.

Doelter (Jahrb. Min. 1886, **1**, 119) found that in absence of steam, a hexagonal $CaSiO_3$ is always formed; hence wollastonite must have been formed in presence of steam. Calcium silicate is therefore dimorphous.

W. Jander and E. Hoffmann (Z. anorg. Chem. 1934, **218**, 211), by heating at 1,000–1,200° powdered mixtures of CaO and SiO_2 in different proportions, for a longer or shorter time, found that $2CaO,SiO_2$ is first formed. For high proportions of CaO ($4CaO$ to SiO_2) and a sufficiently high temperature, $3CaO,SiO_2$ may next be obtained. In other circumstances the next product is $3CaO,2SiO_2$. As heating continues, in the presence of sufficient SiO_2, the final product is CaO,SiO_2.

K. Hild and G. Trömel (Z. anorg. Chem. 1933, **215**, 333) have studied solid reactions between calcium oxide and silicic acid at 1,000°, using equimol. quantities. The time required for completion varies from 5 minutes to 400 hours and is determined by the nature of the reactants and the intimacy of mixing. For reaction times greater than 20 minutes the initial product is β–Ca_2SiO_4, which then reacts with SiO_2 to give β-$CaSiO_3$ (wollastonite). In the most rapid reaction (5 minutes) the main product is α-$CaSiO_3$. In experiments in which quartz was used, the latter was frequently converted into cristobalite in presence of $CaCO_3$, but never in presence of CaO.

Hydrates of Monocalcium Silicate.—E. P. Flint and L. S. Wells (Bur. Stand. J. Res. 1934. **12**, 751) find that the solubility of SiO_2 in solutions of $Ca(OH)_2$ combined with electrometric measurements for saturated and supersaturated solutions indicate the existence of $Ca(H_3SiO_4)_2$, CaH_2SiO_4, $Ca_3(HSiO_4)_2$, and Ca_2SiO_4. The hydrolysis constants of these compounds have been determined, and ionisation constants for the successive stages in the dissociation

of H_4SiO_4 are given as $2{\cdot}2\times10^{-10}$, $2{\cdot}0\times10^{-12}$, 1×10^{-12}, and 1×10^{-12}, respectively. In presence of H_2O, $3CaO{\cdot}2SiO_2$, γ-$2CaO\ SiO_2$, β-$2CaO{\cdot}SiO_2$, and $3CaO{\cdot}SiO_2$, all pass into hydrated forms corresponding with the equilibrium relation of the CaO–SiO_2–H_2O system, but $CaO\ SiO_2$ is unaffected.

R. Nacken and R. Mosebach (Z. anorg. Chem. 1935, 223, 161) state that Ca_3SiO_5 is gradually decomposed by H_2O forming successively with increasing quantities of H_2O, $2CaO,SiO_2,H_2O$, $3CaO,2SiO_2,3H_2O$; and $CaO,SiO_2,2H_2O$. No appreciable dissolution of SiO_2 is indicated. Marked variation in solubility of CaO with fineness of division was observed. The most probable value for the solubility at 20° is 1·2100 g. per litre. By grinding in contact with H_2O a supersaturation of 23% may be obtained.

Calcium Chlorosilicate.—Gorgeu (Compt. rend. 1884, 99, 256) obtained two chlorosilicates by heating to a high temperature silica and calcium chloride in proportion of 1 molecule to 7 in presence of water vapour. The first, $2CaO\ SiO_2\ CaCl_2$, forms birefractive rhombic plates. The second, $CaO{\cdot}SiO_2{\cdot}CaCl_2$, forms hexagonal plates, and is produced more rapidly than the former, which requires prolonged heating. Both compounds are decomposed by water.

Calcium Aluminate.—Nagai and Naito (J. Soc. Chem. Ind. Japan, 1930, 33, 17–19B) prepared calcium aluminate by heating calcium carbonate and alumina in the ratio $3CaO:Al_2O_3$, and the free and combined oxides in the product were determined. At 1,100°–1,250° the primary product is $CaO{\cdot}Al_2O_3$, but at higher temperatures this is converted into $3CaO\ Al_2O_3$, a result similar to those obtained with other ratios (5 : 1 and 3 · 5). A small proportion of the compound $5CaO{\cdot}3Al_2O_3$ was also first formed but eliminated by further heating. The compound $5CaO{\cdot}Al_2O_3$ was also converted by heating into $3CaO{\cdot}Al_2O_3$ with separation of free lime.

S. Nagai and G. Sawayama (J. Soc. Chem. Ind. Japan, 1934, 37, 264B) find that the mixture $4CaO.Al_2O_3{:}Fe_2O_3$ readily forms

$$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3,$$

the *celite* of Portland cement, at 1,250°. A mixture

$$5CaO{:}Al_2O_3{:}Fe_2O_3$$
$$(\text{or } 3CaO{\cdot}Al_2O_3{\cdot}2CaO{\cdot}Fe_2O_3),$$

forms $2CaO\ Fe_2O_3+6CaO{\cdot}Al_2O_3{\cdot}2Fe_2O_3$ (I) at 1,400°–1,420° and $3CaO\ Al_2O_3+$(I) at 1,250°–1,370°. (I) is probably a mixture of $2CaO{\cdot}Fe_2O_3$ and the eutectic (CaO, 47%; Al_2O_3, 53%) between $3CaO{\cdot}Al_2O_3$ and $5CaO\ 3Al_2O_3$.

Rankin and Wright (Amer. J. Sci. 1915, 39, 1) have examined the system CaO–Al_2O_3–SiO_2. The melting-points of the three compounds are 2,570° for lime, 2,050° for alumina and 1,625° for cristobalite, the high temperature modification of silica. Of the binary systems involved alumina and silica form one compound, sillimanite, Al_2SiO_5, whilst lime and alumina form four distinct compounds, $Ca_3Al_2O_6$, $Ca_5Al_6O_{14}$, $CaAl_2O_4$, and $Ca_3Al_{10}O_{18}$. *The third binary system, lime silica, also gives* rise to four compounds, Ca_3SiO_5, Ca_2SiO_4, $Ca_3Si_2O_7$, and $CaSiO_3$, the first mentioned of which, however, does not separate from the fusion. In the ternary system three compounds exist, but only anorthite, $CaAl_2Si_2O_8$, and $Ca_2Al_2Si_2O_{10}$ (? pure gehlenite) are stable at their melting-point, the third, $Ca_3Al_2SiO_8$, being unstable. The above compounds do not form solid solutions to any extent, and the authors did not detect in the crystallisations the eutectic (β) structure commonly seen in alloys

Neuman (Stahl und Eisen, 1918, 38, 953) summarises investigation on the binary and ternary systems of lime, alumina and silica, and points out that possible compositions of slags and Portland cements occupy only very small areas in the triangular diagrams of the ternary mixtures, and refers to the composition and temperature relations for freely flowing slags and general identity with mixtures of pure oxides. With reference to Portland cement, he accepts Rankin's suggestion (J. Franklin Inst 1916, 181) that Portland cement is produced by the formation of the compounds $2CaO,SiO_2$ and $5CaO,Al_2O_3$, which absorb lime and form tricalcic silicate and tricalcic aluminate. The former is regarded as the essential constituent of the cement, the latter acting chiefly as a flux or solvent which reduces the temperature at which the former is produced.

Hydrates of Dicalcium Aluminate.—R. Salmoni (Gazzetta, 1934, 64, 719) has prepared the hydrates $2CaO\ Al_2O_3,nH_2O$, where $n=1$, 3, 6, 10, and 11. Heats of dissolution and X-ray structures of the hydrates with $n=1$, 3, 5, 7, and 9 are given. The higher hydrates will have the same lattice structure as the pentahydrate; this differs from that of the monohydrate.

Travers and Schnoutka (Ann. Chim. 1930, [x], 13, 255) found that interaction of lime water with aluminium nitrate afforded crystalline calcium aluminates, the composition of which varied between $Al_2O_3{\cdot}3CaO,12H_2O$ and $Al_2O_3{\cdot}4CaO,12H_2O$ according to the concentrations employed; the formation takes place in three stages, involving the precipitation of aluminium hydroxide, followed by its dissolution in the lime water as monocalcium aluminate and its precipitation as polycalcium aluminate A similar crystalline polycalcium aluminate is produced from potassium aluminate and lime water. Potassium aluminate reacts in solution with aqueous calcium nitrate containing lime water at p_H 11·57–11·62 to give the pure crystalline $Al_2O_3{\cdot}3CaO,12H_2O$; products expressed by the formula $Al_2O_3{\cdot}3$–$4CaO,12H_2O$ are obtained from the mother-liquors.

Thorvaldson and Grace (Canadian J. Res 1929, 1, 36) obtained tricalcium aluminate by heating alumina with calcium carbonate at 1,370°; it forms the hydrate $3CaO{\cdot}Al_2O_3,6H_2O$ when heated at 150° with steam in an autoclave. This compound forms isotropic crystals, n_D 1·604, which are slightly hygroscopic; at 275°–300° the stable hydrate $(+1{\cdot}5H_2O)$ is formed, and at 1,000° the last traces of water are expelled. At 750°–900° decomposition into free lime and aluminate, $5CaO,Al_2O_3$, occurs, but recombination ensues after heating at above 1,000° or by heating in steam at 150°.

The solubility of the hexahydrate as determined by gravimetric methods is 0·0246 and 0·0268 g. per 100 c.c. at 21° and 40° respectively, whilst the density as determined by displacement in kerosene is 2·522 g. per c.c. X-ray data are tabulated and the crystal structure is described, the lattice constant being 12·576Å $\pm$0·02, with 8 mols. in the unit cube. By exposing the anhydrous aluminate to atmospheres of different humidities at temperatures below 21°, evidence was obtained of the formation of a series of higher hydrates crystallising in hexagonal plates and containing from 8 to 12 mols. of water, but the water is very loosely held, and adsorption of water by the finely crystalline hydrates makes the exact formulæ uncertain. The heats of dissolution in dilute hydrochloric acid (1 : 200) at 20° of the hydrates corresponding with 6, 8, 10, and $12H_2O$ were 519, 489, 482, and 472 g.-cal. per g. respectively, and these differences support the view that a series of hydrates exist, as do the changes in refractive index with degree of hydration. Dehydration of the hexagonal plates at 21° produces no change of shape, however, and the X-ray diffraction patterns of the hydrates with 8, 10, and $12H_2O$ are almost identical.

Pure amorphous calcined and finely ground tricalcium aluminate forms a true colloidal sol in water, an insignificant proportion entering into true solution. The crystal form appears to be highly polymerised, and in contact with water behaves like a colloid (Phillips, J. Amer. Ceram. Soc. 1919, 2, 708).

The hydrated derivatives of the ternary system give rise in nature to zeolites in which, however, the lime is often partly replaced by soda, and the molecular ratio varies from the stilbite molecule, $CaO{\cdot}Al_2O_3{\cdot}6SiO_2,6H_2O$) with decreasing SiO_2 (and generally H_2O) as in mesolite, $CaO(Na_2O){\cdot}Al_2O_3{\cdot}3SiO_2,2H_2O$ to the anorthite molecule, $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ (Thomsonite+$2{\cdot}5H_2O$).

Artificial zeolites in which the composition is given as $CaO(Na_2O){\cdot}Al_2O_3,2SiO_2,6H_2O$ or $CaO(Na_2O){\cdot}Al_2O_3{\cdot}xSiO_2,7H_2O$ are made on a large scale ("permutite," etc.) because of their property of interchange of the Na_2O,CaO molecules in contact with solutions containing the alternate molecule :

$$Na_2O{\cdot}Al_2O_3{\cdot}xSiO_2,yH_2O+CaCl_2 \rightleftharpoons CaO{\cdot}Al_2O_3{\cdot}xSiO_2,yH_2O+2NaCl$$

Hydrated Calcium Sulphatoaluminate and Calcium Chloroaluminate.—J. Lefol (Compt. rend. 1934, 198, 1858) by thermal analysis shows that: (i) $Al_2O_3{\cdot}3CaO{\cdot}3CaSO_4,30H_2O$ rapidly loses H_2O on heating, forming a heptahydrate stable at 145° and decomposed at higher temperature; free $CaSO_4$ is not liberated; (ii) $Al_2O_3{\cdot}3CaO{\cdot}CaCl_2,10H_2O$ (I) is stable to 120° and forms a hexahydrate at 175° which is stable to 280°. At temperature $>$100° (I) decomposes to $CaCl_2+Al_2O_3{\cdot}3CaO$.

Aqueous $CaCl_2$ reacts fairly rapidly with $3CaO{\cdot}Al_2O_3$ at 30°, forming the compound, $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2,10H_2O$. This reaction controls the influence of $CaCl_2$ on the setting of Portland cement (R. Nacken and R. Mosebach, Z. anorg. Chem. 1936, 228, 19).

System Iron–Iron Oxide–Calcium Orthoferrite.—E. Martin and R. Vogel (Arch. Eisenhüttenw. 1934–1935, 8, 249) show that thermal and micrographic observations have disclosed two compounds, $CaO{\cdot}9FeO$ (I), m.p. 1,310°, and $4CaO{\cdot}3Fe_3O_4$, m.p. 1,200°. The system may be divided into five 3-phase fields and one 2-phase field, the other solid phases present being Fe, Fe_3O_4, wüstite, $CaFe_2O_4$, and $Ca_2Fe_2O_5$. Eutectics are formed at Fe_2O_3 62·8, CaO 26·9, Fe 10·3%, 1,110° [(I)+$Ca_2Fe_2O_5$]; Fe_2O_3 65·3, CaO 25·8, Fe 8·9%, 1,120°; and Fe_2O_3 72·0, CaO 24·5, Fe 3·5%, 1,240° (Fe_3O_4+$Ca_2Fe_2O_5$). Free Fe occurs in the melts when the Fe content is greater than that corresponding with the sections (I)–$Ca_2Fe_2O_5$ and (I)–wüstite.

S. Nagai and T. Yoshiura (J. Soc. Chem. Ind. Japan, 1935, 38, 374B) find that $CaO{\cdot}Fe_2O_3$ and $2CaO{\cdot}Fe_2O_3$ are formed by heating a mixture $2CaO+Fe_2O_3$ at 1,000°–1,100° and 1,200° respectively. Addition of 1% of CaF_2 lowers the temperature of formation by 50°–100° (*e.g.* reaction is completed after one hour at 1,100°).

Calcium Boride, CaB_6, was obtained by Moissan (Compt. rend. 1897, 125, 629 ; 1902, 134, 137) by heating quicklime with boron in an electric furnace, and by reducing calcium borate with aluminium in the presence of carbon, then washing with hydrochloric and hydrofluoric acids and ether. It is a black crystalline body ; sp.gr. 2·33. Nitric acid attacks it vigorously.

It is also formed (Ber. 1912, 46, 1885) when calcium metaborate (30 g.) is reduced by means of calcium (50 g.), the theoretical quantity of calcium boride being produced. The reaction product is extracted with dilute acetic acid, and then dilute HCl and hot water. So obtained it is a light brown micro-crystalline powder d^{18} 2·11.

Calcium Borate occurs in nature in several combinations. The best known is colemanite, $HCa(BO_2)_3,2H_2O$, which crystallises in beautiful monoclinic prisms.

Calcium Silicoborate, $CaO{\cdot}2SiO_2{\cdot}CaB_2O_4$, occurs with one molecule of water as datolite, and with two molecules of water as botryolite.

Calcium Titanate, $CaTiO_3$, occurs in nature as perovskite.

Calcium Silicotitanate, $CaSiTiO_5$, is a common constituent of many igneous and metamorphic rocks, and is known as titanite, or sphene. Synthetic titanite forms blue crystals (m.p. 1,221°), which usually enclose small crystals of perovskite (Z. anorg Chem. 1911, 73, 293).

Calcium Monosulphide, CaS. Perfectly dry lime remains unaltered on passing over it a current of dry sulphuretted hydrogen; but on hydrating the lime and again passing the gas, calcium sulphide is formed :

$$Ca(OH)_2+H_2S=CaS+2H_2O$$

The most favourable temperature is 60° (Veley, J.C.S. 1885, 47, 478). It may also be prepared by heating the sulphate with coal or charcoal, or by the action of carbonic oxide at a red heat :

$$CaSO_4+4CO=CaS+4CO_2$$

It may be prepared in the crystalline state by direct reduction of the sulphate with carbon in the electric furnace; Müller (Cent. Min. 1900, 178) has obtained it in small cubes.

Rodriguez Mourelo (Compt. rend. 1915, 161, 172) prepared calcium sulphide by heating 100 g. $CaCO_3$, 0·1 g. NaCl, 0 03 g. Na_2CO_3, flowers of sulphur and the necessary active amounts of Mn compounds, amounts varying from 0·1 to 0 0001% of Mn to $CaCO_3$ taken. The temperature of heating was 300°–1,000°, and the time 4 hours All the specimens thus prepared showed marked phototropy but no phosphorescence. Under the influence of light the colours assumed were shades of red or violet, and in one case a shade of yellow, the maximum intensity being quickly attained.

Anhydrous calcium sulphide is a white powder which emits an odour of H_2S in the air. It turns yellow on moistening, due to the formation of oxidised products It is only sparingly soluble in water, and is decomposed by boiling water, with formation of hydroxide and sulphydrate of calcium :

$$2CaS+2H_2O=Ca(HS)_2+Ca(HO)_2$$

A suspension in water is readily decomposed by carbon dioxide, with formation of calcium carbonate and sulphuretted hydrogen :

$$CaS+H_2O+CO_2=CaCO_3+H_2S$$

After being heated, calcium sulphide shines in the dark, and was long known as *Canton's phosphorus*

According to Verneuil (Compt rend. 1886, 103, 600), calcium sulphide with a violet phosphorescence may be prepared as follows: 20 g. of finely powdered lime, obtained by heating the shells of *Hypopus vulgaris*, is intimately mixed with 6 g of sulphur and 2 g. of starch, and 8 c c. of a solution containing 0 5 g. basic bismuth nitrate and 100 c c. of absolute alcohol acidified with a few drops of hydrochloric acid. The mixture is exposed to the air until most of the alcohol has evaporated, and is then heated to cherry redness for 20 minutes. When completely cooled, the upper layer of calcium sulphate is removed, and the calcined mass powdered and again heated for 15 minutes. The violet phosphorescence of the product is due to the trace of bismuth. 0·1% of sulphides of antimony, cadmium, mercury, tin, copper, lead, uranium, platinum or zinc imparts a bluish- or yellowish-green tint to the phosphorescence Manganese produces an orange shade. A mixture of 100 parts lime, 30 parts sulphur, 10 parts starch, and 0 035 part lead acetate yields a sulphide with a beautiful yellowish green phosphorescence.

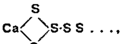
Pure calcium carbonate mixed with 2% sodium carbonate, and 0 02% common salt, heated with 30% sulphur and 0 02% bismuth nitrate, yields a similar product to that obtained by use of hypopus shells Pure calcium sulphide does not phosphoresce (J. H. Frydlender, Rev. Prod. chim. 1930, 33, 723, 757 ; 1931, 34, 5). The phenomenon is due to small quantities of impurities ; thus in the last mixture it has been shown by Verneuil to be due to simultaneous presence of traces of bismuth oxide, sodium carbonate and chloride and calcium sulphate

These phosphorescing varieties of calcium sulphide are utilised in the manufacture of luminous paints. Abney (Phil. Mag. (5), 13, 212) found that the emission spectrum showed greatest luminosity between G and F, and a feebler one extending from between E and F as far as the red. The rays of the electric light somewhat beyond H on one side and G on the other are most active in exciting phosphorescence.

Calcium Disulphide, CaS_2, is deposited in yellow crystals of the composition $CaS_2,3H_2O$ from the solution obtained by boiling sulphur with milk of lime and filtering while hot.

Calcium Pentasulphide, CaS_5, is formed when the monosulphide or hydrate of calcium is boiled for a long time with excess of sulphur Concentrated solutions of calcium hydrosulphide, $Ca(HS)_2$, also react energetically upon powdered roll sulphur; on preventing access of air by performing the operation in a current of hydrogen, an orange-red solution is produced with a fall of temperature, and on warming the calcium is completely converted into CaS_5 The reaction is reversible, a current of sulphuretted hydrogen causing deposition of sulphur and reformation of hydrosulphide (Divers and Shimidzu, J.C S 1884, 45, 270).

Auld obtained evidence indicating the possible existence of polysulphides as high as CaS_7, and suggests the constitution



the atoms of sulphur in the chain becoming progressively more loosely attached (Auld, J.C.S. 1915, 107, 480). (For the chemical composition of lime-sulphur animal dips, see Chapin, U.S.A. Dept. Agric. Bull. 451, 1916)

Calcium Oxysulphides,

$$CaS_5,5CaO,20H_2O.$$

This oxysulphide is obtained in gold-coloured needles when a solution of crude calcium monosulphide is evaporated (Rose, Annalen, 1842, 44, 241).

According to Hoffmann (Compt. rend. 1866, 62, 291) a mixture of two molecules of calcium monosulphide and one molecule lime at a red heat forms the oxysulphide 2CaS CaO. This oxysulphide is also contained in recently lixiviated soda residues.

Geuther (Annalen, 1884, 224, 178) obtained crystals of $CaS_3 \cdot 2CaO,10H_2O$ by boiling sulphur in milk of lime. They dissolve in hydrochloric acid, forming hydrogen persulphide, H_2S_3, and a little H_2S. On boiling calcium monosulphide and sulphur with water, crystals of $CaS_3 \cdot 3CaO,15H_2O$ were obtained. Divers obtained a compound of the formula

$$11CaS \cdot 5CaO$$

by igniting lime in a mixture of carbon dioxide and carbon disulphide.

Auld (J.C S. 1915, 107, 480), by boiling together lime and sulphur in proportions cal

culated to give the disulphide, obtained in each case Herschell's crystals, for which he proposes the formula $CaO,CaS_2,7H_2O$. A lime-sulphur wash, used as a fungicide, is prepared by boiling together 1 part of quicklime, 2 or more parts of sulphur, and 10 parts of water. The concentrated commercial product contains calcium polysulphides and thiosulphate, generally with minor proportions of sulphite and sulphate.

Winter (Ind. Eng. Chem. 1918, **10**, 539) found that lime-sulphur solution prepared from ordinary common lime and sulphur which has been standing for several days does not contain any appreciable amounts of hydrogen sulphide, calcium hydrosulphide, or calcium hydroxy-hydrosulphide; free calcium hydroxide is not present, as any excess of $Ca(OH)_2$ originally present or added disappears gradually. The orange-red crystals which separate from lime-sulphur solution have the composition

$$2CaO,CaS_3,11H_2O.$$

Calcium Sulphydrate, $Ca(HS)_2$, is formed together with the hydroxide when the mono-sulphide is boiled with water. The best mode of preparing it is to pass sulphuretted hydrogen through the hydroxide or sulphide suspended in water, with constant agitation, until it ceases to be absorbed. It is difficult to obtain in the solid stage, being decomposed, when the stage of crystallisation is reached, into H_2S and CaS which separates in silky prisms.

Divers (J.C.S. 1884, **45**, 270) obtained it in the solid form by forcing sulphuretted hydrogen through semi-solid calcium hydroxide and water so as to obtain a saturated solution of the sulphydrate. Air was excluded, and, on settling, decanting in a stream of H_2S, and cooling by ice, crystals formed in abundance. They were colourless prisms, melting on slight rise of temperature with partial decomposition. They readily dissolved in one-fourth of their weight of water, and could not be removed from the atmosphere of sulphuretted hydrogen without decomposition. They possessed the formula $Ca(SH)_2,6H_2O$.

Calcium sulphydrate may be used as a depilatory, and for this purpose it is prepared in the form of a paste by passing sulphuretted hydrogen into thin milk of lime until the mass acquires a bluish-grey colour. It has been employed in the tan-yard.

Calcium Hydroxy-Sulphydrate, $Ca(SH)(OH)$, is formed, according to Divers, by the action of water upon the crystals of the last-described salt: $Ca(SH_2)+H_2O=Ca(SH)(OH)+H_2S$. Also by union of water with calcium sulphide, as in interior of heaps of soda waste; and by reaction between $Ca(OH)_2+H_2S$ in the coal-gas purifier. Exposed to air, crystals of $Ca(HS)_2$ are rapidly converted to $Ca(SH)(OH)$, and concentrated solutions of the sulphydrate exposed to air become rapidly covered with crystals, and an abundant crop of crystals of $Ca(SH)(OH)$ is obtained on passing in a current of air. The crystals are colourless four-sided prisms of silky lustre, easily obtained dry, of the composition

$$Ca(SH)(OH),3H_2O.$$

They slowly evolve H_2S in air, and become yellow by adsorption of oxygen. They are readily soluble in water, but the solution rapidly decomposes into hydroxide and sulphydrate. They are insoluble in alcohol.

According to Folkard (Chem. News, 1884, **49**, 258), by exposing calcium hydroxide to the action of sulphuretted hydrogen until it ceases to gain weight a grey powder of the composition $4Ca(OH)_2{\cdot}3H_2S$ is obtained; this evolves sulphuretted hydrogen by the action of coal gas, and at 100° water is eliminated, leaving $Ca(OH)_2{\cdot}Ca(SH)(OH)$. This greyish-green powder, when gently heated in coal gas, leaves a yellowish-white salt,

$$2Ca(OH)_2{\cdot}Ca(SH)(OH){\cdot}CaS,$$

which, at a red heat, forms

$$2CaO{\cdot}Ca(SH)(OH){\cdot}CaS,$$

and this, when ignited in air, burns like tinder to $CaSO_4$.

The lime-sulphur solutions employed as insecticides and plant-sprays in agriculture, prepared by boiling together water, lime, and sulphur, consist mainly of calcium polysulphides, calcium hydroxysulphydrate, calcium thio-sulphate with sulphur held in solution. For their analyses, *see* Bodnár (Chem. Zeit. 1915, **39**, 715; Analyst, 1915, **40**, 513); Ramsay (J. Agric. Sci. 1915, **6**, 476). The following is an analysis of a typical lime-sulphur spray, sp.gr. 1·3735, the results being expressed in g. per 100 c.c. (Ramsay, *l.c.*):

	Sulphur.	Calcium as CaO.
Hydroxy-sulphydrate .	0·944	1·653
Disulphide	14·716	12·877
Free sulphur . . .	23·11	—
Thiosulphate . . .	0·99	0·86
Sulphate	0·07	0·11
	39·83	15·50

Calcium Sulphocarbonate, $CaCS_3$.—Lime over which coal gas containing sulphuretted hydrogen has been passed readily adsorbs carbon disulphide. Adsorption is most complete when the lime is moistened with water; the "fouled" lime is then mixed with an equal weight of slaked lime. The adsorption of carbon disulphide stops when one-third of the sulphide is converted to sulphocarbonate, $CaS+CS_2=CaCS_3$. On exposing the product for a short time to the air, it is again rendered capable of removing carbon disulphide.

On passing hydrogen saturated with vapour of carbon disulphide into a mixture of calcium monosulphide and a little water, the liquid becomes red, and in vacuo deposits red prismatic very deliquescent needles of the composition, $Ca(OH)_2{\cdot}CaCS_3,7H_2O$. When the hydroxy-sulphydrate is employed instead of monosulphide, yellow crystals of

$$2Ca(OH)_2{\cdot}CaCS_3,10H_2O$$

are obtained.

From these facts Veley (J.C.S. 1885, 47, 478) concludes that the carbon disulphide is adsorbed by $Ca(SH)(OH)$, and not by CaS, and that the reactions are as follows:

$$(1)\ CaS+H_2O=Ca(SH)(OH)$$

$$(2)\ Ca(SH)_2+H_2O=Ca(SH)(OH)+H_2S$$

$$(3)\ 2Ca(SH)(OH)+CS_2 =Ca(OH)_2 CaCS_3+H_2S$$

The basic sulphocarbonate is unstable, being decomposed slowly by sulphuretted hydrogen and readily by carbon dioxide.

When milk of lime is agitated with carbon disulphide, bright orange needles of a basic sulphocarbonate, $Ca(OH)_2 CaCS_3,6H_2O$, are deposited.

Calcium Selenides. The monoselenide is formed as a flesh-coloured precipitate by precipitating calcium chloride with potassium monoselenide. Lime water saturated with seleniuretted hydrogen deposits crystals of calcium selenide on spontaneous evaporation When lime and selenium are heated just below redness, a polyselenide mixed with calcium selenide is formed

Calcium Sulphite, $CaSO_3$, is formed when a solution of an alkaline sulphite is added to the solution of a calcium salt it is a white powder soluble in 800 parts of water. It dissolves in sulphurous acid, and the solution yields six sided needles of the composition $CaSO_3,2H_2O$

The solution in sulphurous acid known commercially as bisulphite of lime, and manufactured by passing sulphur dioxide into milk of lime, is largely used in the manufacture of sulphite cellulose.

According to Birnbaum and Wittich (Ber 1880, 13, 651), calcium oxide does not adsorb sulphur dioxide gas below 400°, but at this temperature combination takes place rapidly with formation of a basic sulphite, $Ca_6S_5O_{16}$ or $6CaO\ 5SO_2$ At 500° the gas is rapidly adsorbed, but the sulphite splits up into sulphate and sulphide

Briner and Monnier (Helv Chim Acta, 1930, 13, 80–85) find that no action even after months of contact can be observed between sulphur dioxide in the gaseous or liquid states and dry calcium carbonate at the ordinary temperature. A relatively rapid reaction represented by

$$2CaCO_3+3SO_2 =2CaSO_4+S+2CO_2+74\ \text{kg-cal.}$$

occurs at 95°. If water is present sulphite is formed by simple replacement.

Calcium Sulphate, $CaSO_4$, occurs in solution in sea-water or rivers and is found abundantly in deposits as gypsum, $CaSO_4,2H_2O$, of which the well crystallised form is termed *selenite*, a fibrous variety *satin-spar*, and a marble-like form *alabaster* (*q v*).

Hydrated calcium sulphate is precipitated on adding dilute sulphuric acid or a soluble sulphate to an aqueous solution of calcium chloride. The sp gr. of gypsum is 2 31. When it is heated to 100°–200° it gives up three-fourths of its water rather quickly, but it requires a temperature of 200°–250° to expel the remainder. Dried at 100°, the hemihydrate

$$2CaSO_4,H_2O$$

of sp gr. 2·7 is left. The anhydrous salt fuses at a red heat without decomposition, and on cooling assumes the structure of anhydrite (*q.v.*). When the hemihydrate is pulverised and mixed with water, it adsorbs 3 molecules of water, and solidifies to a very hard mass with evolution of heat, expanding so as to fill any mould in which it is cast, due probably to the outward thrust of the lath-shaped crystals of the hydrated salt during growth; hence the use of gypsum or plaster of Paris in preparing casts (*see* BUILDING MATERIALS, Calcium Sulphate Plasters and Cements).

Grengg (Z. anorg. Chem. 1916, 90, 327) prepared the hemihydrate $CaSO_4,\frac{1}{2}H_2O$ by digesting gypsum with warm HNO_3. It forms hexagonal prisms. Large crystals are obtained by heating gypsum with concentrated $NaCl$ solution at 80°–100°. The hexagonal form is only apparent, the crystals are rhombic, repeatedly twinned

Hydrated calcium sulphate, gypsum, is soluble in water, the solubility attaining a maximum at 35°, 1 part dissolving in 393 parts water (Poggiale), at 0° in 488 parts, and at 100° in 460 parts The solubility is increased by the presence of hydrochloric or nitric acids, or chlorides of ammonium or sodium, hence its presence in salt springs; probably in most cases partial double decomposition has occurred.

According to Lunge (J.S C I 1885, 4, 31), the solubility of calcium sulphate in solutions of sodium chloride increases with the percentage of salt, but diminishes with increase of temperature The quantity of calcium sulphate dissolved by 100 c c of the salt solution is shown in the following table:

Temp. °C.	21 5	18 0	101 0	102 5
$NaCl$ % .	3 53	14·18	3 53	14 18
$CaSO_4$ g.	0 5115	0·7340	0 4891	0 6249

Calcium chloride diminishes the solubility of $CaSO_4$ the more it is concentrated, but at the boiling point the concentration is immaterial Hydrochloric acid increases the solubility both with increase of concentration and of temperature.

Gypsum is readily soluble in excess of sodium thiosulphate, forming calcium thiosulphate, which combines with the excess of the sodium salt to form a soluble double thiosulphate. On addition of alcohol, this double salt separates as a heavy thick liquid, which solidifies, forming needle shaped crystals.

The reaction between gypsum and carbon sets in below 300°, but very slowly, and is fairly rapid from about 700° and upwards; under suitable conditions pure CaS is obtained:

$$CaSO_4+3C=CaS+CO_2+2CO$$

Similarly, with strontium and barium the sulphides are formed, the differences in behaviour being accounted for by a consideration of the heats of reaction. The reaction

$$CaS+H_2O+CO_2\rightleftarrows CaCO_3+H_2S$$

cannot be used for the profitable conversion of calcium sulphide.

Calcium and barium sulphate can be conveniently and quantitatively reduced by CO at a temperature of 900°–950° (Hofman and Mostowitsch, Amer. Inst. Min. Eng. 1910, **917**, 939). The sulphate is first rendered anhydrous by heating until weight is constant; the reduction commences at 680°–700°, becomes vigorous at 750°–850°, and is practically finished at 900°. The heating is continued until there is no further loss. With carbon in an atmosphere of nitrogen decomposition begins at 700°, it is vigorous at 800°–900°, and complete at 1,000°. By oxidation of CaS in dry air, the action begins at 800°, yielding 73% $CaSO_4$ and 27% CaO.

A large scale process in Germany, for utilising the dumps of calcium sulphate resulting from the neutralisation of excess sulphuric acid in sulphonation processes, consists in mixing the press-cake with coal and a slagging material, presumably of the composition required to give a cement mixture; this is fed into a rotary kiln 50 m. long and 3 m. in diameter which is fired by coal-dust. The fumes containing sulphur dioxide are cleaned from dust by electrostatic means and are passed into the sulphur trioxide converters. The cement produced from the clinker is of satisfactory quality (Allmand and Williams, J.S.C.I. 1919, **38**, 287R).

Preparations of gypsum could not be completely dehydrated at 115°. The water of crystallisation was never reduced to less than 4%. The common dihydrate lost its crystal water at 102° more slowly and less completely than other forms (Neugebaur, Kolloid-Z. 1922, **31**, 40).

Burnt gypsum may be regarded as consisting of two components, one soluble, which dissolves quickly, and the other relatively insoluble. The solution of samples which have been burnt at 500°–800° is rapid at first, this being explained by the presence of appreciable proportions of soluble modification of dead burnt gypsum.

Samples of $CaSO_4$ were heated to constant weight at temperatures of 800°–1,375°, and the proportion of CaO in the products determined: at 1,000°, 0·21 CaO; at 1,300°, 3·0 CaO; and at 1,375°, 98·67 CaO. Above 1,300° the salt melts and vigorous evolution of fumes take place (Budinov and Syrkin, Chem.-Ztg. 1923, **47**, 32).

$CaSO_4$, when melted in the electric furnace, gives a f.p. 1,450°, and transformation point 1,193° (Grahmann, Z. anorg. Chem. 1913, **81**, 257).

Sulphur dioxide is prepared on a large scale by sintering gypsum with sand in a rotating furnace, the residue being used as cement (Gallo, 1928, B. 12). For the manufacture of ammonium sulphate from gypsum, see Vol. I, 350.

Acid Calcium Sulphate, $CaSO_4{\cdot}H_2SO_4$, is formed by heating the neutral sulphate with strong sulphuric acid to 80°–100°. A portion of the porous mass produced dissolves and separates on cooling in microscopic prisms of the composition above indicated. It is decomposed by water, even the moisture of the air, into gypsum and sulphuric acid.

Calcium-Sodium Sulphate, $CaNa_2(SO_4)_2$, occurs native in rhombic prisms as the mineral *glauberite*. It may be obtained in the same form by fusing together calcium and sodium sulphates. On heating 50 parts sodium sulphate (Glauber's salt) with an emulsion of 1 part gypsum in 25 parts water to 80°, crystalline needles of $CaSO_4{\cdot}2Na_2SO_4,2H_2O$, are deposited. On further heating, these crystals are transformed into microscopic monoclinic crystals of glauberite.

In the Welsh process of manufacturing sodium acetate, during evaporation of the liquor formed by double decomposition of calcium acetate by sodium sulphate, micaceous spangles of glauberite have been observed to separate out (Folkard, Chem. News, 1881, **43**, 6). This explains why calcium sulphate so tenaciously retains sodium sulphate.

Calcium Potassium Sulphate,

$$CaSO_4{\cdot}K_2SO_4,H_2O,$$

occurs native in monoclinic crystals as *syngenite*. It is formed by mixing solutions of the two salts. When a mixture of equal weights of anhydrous calcium sulphate and potassium sulphate is stirred up with less than its weight of water, the mass suddenly solidifies. If 4–5 parts of water are used, the solidification is not quite so rapid, but gives casts superior to those of plaster of Paris, inasmuch as they possess a polished surface.

A salt of the composition

$$CaSO_4{\cdot}K(NH_4)SO_4,Aq.,$$

is obtained by adding an excess of potassium sulphate to a warm concentrated solution of ammonium sulphate which has been saturated with calcium sulphate. The same salt is formed when the double sulphate of calcium and potassium is treated with a warm solution of ammonium sulphate (Fassbender, Ber. 1878, **11**, 1968).

Calcium Persulphate. The salt may be extracted by means of absolute ethyl alcohol from the dried mixture resulting from the action of ammonium persulphate on calcium hydoxide (Erdenbrecher, Chem.-Ztg. 1924, **48**, 189).

Calcium Thiosulphate, $CaS_2O_3,6H_2O$, is prepared by heating a suspension of calcium sulphite and sulphur in water. Divers (J.C.S. 1884, **45**, 270) obtained it by oxidation of calcium sulphydrate in a current of air, calcium hydroxysulphydrate being first formed:

$$Ca(SH)(OH)+2O_2+H_2S=CaS_2O_3+2H_2O$$

It forms triclinic prisms soluble in their own weight of cold water. On heating the solution to 60°, it is decomposed with deposition of sulphur. It is used for the preparation of antimony cinnabar, Sb_2OS_2, a pigment for oil paints.

P. Petrovici (J. Pharm. Chim. 1934, [viii], **19**, 392) shows that $CaS_2O_3,6H_2O$ is stable at 18° when the H_2O v.p. is 9–12 mm. It loses $5H_2O$ when kept over 50% H_2SO_4 or heated at 30°; above 80° decomposition to $CaSO_3$, S, and H_2O commences.

Calcium Chromate, $CaCrO_4,4H_2O$, is prepared by dissolving calcium carbonate in aqueous chromic acid, or as a light yellow precipitate on mixing concentrated solutions of calcium chloride and potassium chromate. Bourgeois (Jahresber. Min. 1880, 1 Ref 351) prepares the anhydrous salt by heating to bright redness 2 molecules of the chloride with 1 molecule of potassium chromate and 1 of sodium carbonate It forms slender yellow needles, moderately soluble in water. The hydrated salt gives up its water at 200°, and the anhydrous salt is used as a pigment.

The acid chromate $CaCr_2O_7,3H_2O$ is obtained in red deliquescent crystals by evaporating a solution of the neutral salt in aqueous chromic acid

Calcium Potassium Chromate,

$$(CaK_2)(CrO_4)_2Aq\,,$$

forms yellow silky needles, obtained by saturating acid potassium chromate with calcium hydroxide

For *Detection and Estimation of Calcium*, *see* CHEMICAL ANALYSIS G. S B.

CALCIUM-SANDOZ is calcium gluconate (9 3% **Ca**) Used in calcium therapy (Sandoz, London ; Brooks and Warburton, London), B P.C. 1934

CALCO-URANITE *v.* AUTUNITE.

CALEDON COLOURS *v.* ANTHRAQUINONE DYESTUFFS

CALENDULA OFFICINALIS, Marigold (Fam. Compositæ), contains a saponin the aglucone of which is oleanolic acid (Winterstein and Stein, Z physiol Chem 1931. 199, 64).

CALGON. Sodium hexametaphosphate, $Na_2(Na_4P_6O_{18})$ Scouring and water softening agent, removing calcium in the form of the soluble salt $Na_2(Ca_2P_6O_{18})$ which does not yield calcium ions

CALIATUR WOOD. This wood is very similar to, though somewhat darker in colour than, sanderswood It was imported from the East Indies and is stated to have been chiefly employed on the Continent. According to Franchimont and Sicherer it contains santalin but in larger amount than sanderswood (Ber. 1879, 12, 14) (*v.* BARWOOD).

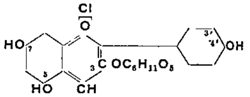
CALICHE. The term by which the impure native sodium nitrate or Chile saltpetre is known throughout South America. Also applied to a limestone hardpan found in Arizona and elsewhere.

CALIFORNITE. A variety of Vesuvianite

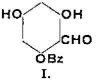
CALISAYA or YELLOW BARK. A variety of cinchona bark.

CALLISTEPHIN. One of the anthocyanin pigments of purple-red asters (*Callistephus chinensis* Nees, syn. *Aster chinensis* Linn), which was isolated as a hydrochloride, $C_{21}H_2,O_{10}Cl,2\frac{1}{2}H_2O$, by Willstätter and Burdick (Annalen, 1916, 412, 149), after separation from asterin chloride by fractional precipitation from alcohol by ether and recrystallisation from aqueous hydrochloric acid. The fine orange red needles are easily soluble in water, alcohol or dilute **HCl** or H_2SO_4, and give a dull violet red colour with sodium acetate and violet red with sodium carbonate and sodium hydroxide. Since there are not adjacent hydroxyls at 3′ and 4′, ferric chloride gives no colour reaction The high distribution number (partition value between amyl alcohol and aqueous **HCl**) which is increased by dilution, is normal for a monoglucoside Hydrolysis yields pelargonidin (1 mol.) and glucose (1 mol).

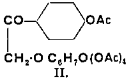
The position of this glucose molecule at 3 was confirmed when Robertson and Robinson (J C S 1928, 1460) obtained the chloride of the first synthetic natural anthocyanin, pelargonidin 3 β monoglucoside, which was identical with callistephin chloride.



The synthesis depends upon the condensation of the O tetra-acetyl β glucoside (II) of the carbinol, $AcO\ C_6H_4\ CO{\cdot}CH_2{\cdot}OH$, with O benzoyl phloroglucinaldehyde (I) in a mixture of ether and chloroform, and subsequent hydrolysis with cold 8% aqueous sodium hydroxide, and acidification ·



I.



II.

In the Chinese Aster, Witt (Dissertation, Groningen, 1936) has shown that pigmentation by callistephin is recessive both to that by the corresponding pelargonidin 3 5-diglucoside and also to that by the more oxidised cyanidin and delphinidin types (*see* CHRYSANTHEMIN) This follows the general rules of dominance put forward by Scott-Moncrieff (J. Genetics, 1936, 32, 117), whereby the pelargonidin 3 monoside pigmentation in pale salmon and coral pink flowers of different species is apparently always the bottom recessive anthocyanin type. R. S ·M

CALLITROPIC ACID. A crystalline acid, $C_{20}H_{30}O_3$, m p 263°, was extracted from sandarac resin by Rollett (Monatsh. 1928, 50, 1)

CALLUTANNIC ACID was obtained by Rochleder by alcoholic extraction of heather (*Calluna vulgaris, Erica vulgaris*) followed by preparation of the lead salt and its decomposition by H_2S ; he gave it the formula

$$C_{14}H_{12}O_8+H_2O\ (I)$$

(Sitzungsber Akad. Wiss Wien, 1852, 9, 286: 1866, 53, 369 ; Annalen, 1852, 84, 354). Thal's analysis did not agree with this formula (Ber. 1883, 16, 1502) Rochleder describes the substance as dyeing wool mordanted with alum deep yellow. A. G. Perkin and F. Newbury (Proc. Chem. Soc. 1899, 15, 179) state that heather contains the colouring matter quercetin and that

a catechol tannin is present in small quantity. It is doubtful whether (I) has been prepared in a pure state.

CALMATAMBIN, $C_{19}H_{28}O_{13},2H_2O$, m.p. 144°, $[\alpha]_D$ −130°, found in the bark of *Canthium glabriflorum* Hiern. from Sierra Leone, crystallises in colourless prismatic needles. It is hydrolysed by mineral acids and by emulsin to glucose and *calmatambetin*,

$$MeO \cdot C_{12}H_{10}O_2(OH)_5.$$

It is physiologically inactive (Pyman, J.C.S. 1907, **91**, 1228), and has not been further investigated.
E. F. A.

CALMONAL. Double salt of urethane and calcium bromide, m.p. 107°,

$$(C_2H_5 \cdot CO_2NH_2)_4 \cdot CaBr_2,2H_2O,$$

has hypnotic properties (Gehe & Co.).

CALOMEL. Mercurous chloride.

CALOMELOL. A colloidal preparation of calomel containing 20% of albuminoids (" U.S. Dispensatory," 20th ed., p. 1300).

CALONCOBA GLAUCA, CALONCOBA ECHINATA, ONCOBA WELWITSCHII. (1929, B., 870.) Antileprosy oils in Brazil and the Cameroons (Peirier, J. Pharm. Chim. 1929, **10**, [viii], 124 ; Perrott and François, Bull. Sci. Pharmacol. 1929, **36**, 551).

CALOPHYLLUM INOPHYLLUM Linn. A tree (Fam. Guttiferæ), Alexandrian laurel, dilo of Fiji, and sultana champa of Bengal, the nuts of which yield 58% of a green, semi-solid oil clearing at 50°, containing the following acids: palmitic (14·1%), stearic (11·0%), erucic (3·0%), oleic (48·0%), linoleic (14·3%), resin acids (9·7%), together with unsaponifiable matter (0·25%) containing sitosterol (Glasgow, J.S.C.I. 1932, **51**, 172).

CALOTYPE. A photographic process patented by Fox Talbot in 1841, in which sensitised paper containing silver iodide was exposed in a camera.

CALUMBA ALKALOIDS. Calumba root, Calombæ radix, is indigenous to East Africa. Syn. are the following terms: *Jateorhiza Calumba*, *Cocculus palmatus*, *Menispermum palmatum*, *Chasmanthera palmata*. The plant, which belongs to the Fam. Menispermaceæ, is also grown in Madagascar, Ceylon, and in the East Indies. Extracts of Calumba root are official in the British Pharmacopœia, B.P.C., 1934. Calumba root is no longer official in the United States Pharmacopœia, 1936.

Jateorhiza Calumba contains three quaternary alkaloids—palmatine (I), jatrorrhizine (II), columbamine (III)—and two glucosides—columbin and chasmantherin. For early literature, *see* Gadamer (Arch. Pharm. 1902, **240**, 450 ; *ibid.* 1906, **244**, 255), Günzel (*ibid.* 1906, **244**, 257), Feist (*ibid.* 1907, **245**, 586 with early references), and Feist and Sandstede (*ibid.* 1918, **256**, 1). The early history of these alkaloids is somewhat confusing : Günzel (*l.c.*) isolated a base columbamine, Feist (*l.c.*) found palmatine and jatrorrhizine (called jateorrhizine in earlier papers), but it was Späth and Duschinsky (Ber. 1925, **58**, [B], 1939) who showed that Günzel's and Feist's base columbamine was really palmatine. Späth and Burger (Ber. 1926, **59**, [B], 1486) isolated a third alkaloid for which the term columbamine was used. References concerning columbamine earlier than 1926 should therefore be applied to palmatine.

According to Späth and Duschinsky (*l.c.*) the roots are extracted with EtOH, the EtOH-residue is extracted with very dilute acid, and the total alkaloids precipitated with HI. The crude crystalline iodides are fractionated with K_2CO_3 and KOH when (I)-iodide is left behind. The separation of the quaternary phenolic bases is difficult and they are best reduced to the tetrahydro-compounds with H_2SO_4 and zinc, or amalgamated zinc + 30% acetic acid (Awe, Ber. 1934, **67**, [B], 836), or zinc and acetic acid (Feist, Awe and Etzrodt, Arch. Pharm. 1934, **272**, 817). The crude tetrahydrobases are fractionated with HCl ; the first fractions deposit a sparingly soluble hydrochloride which is converted into the free base tetrahydrojatrorrhizine (V). From the mother-liquors an easily soluble chloride was isolated and converted into the free base tetrahydrocolumbamine (VI). The total yield of crude iodides is about 4·3% (Feist and Dschu, Arch. Pharm. 1925, **263**, 294) of which 2% is (I)-iodide. According to Späth and Duschinsky (*l.c.*) 32 g. of the crude quaternary phenolic iodides yield 18 g. of the crude tetrahydro mixture. The yield of (VI) is very small; Späth and Burger (*l.c.*) isolated 0·52 g. from 30 g. crude quaternary bases.

Palmatine (I)-iodide, $C_{21}H_{22}O_4NI+2H_2O$, m.p. 240°, crystallises from H_2O in yellow needles ; (I)·Cl yellow needles, m.p. 205° ; (I)·NO_3, m.p. 239°, greenish-yellow needles. (I) is easily reduced to rac. tetrahydropalmatine (IV), m.p. 144°, colourless glistening leaflets. (IV)·HCl is sparingly soluble. The *d*-form of (IV) occurs in Corydalis roots. The great similarity of (I) to berberine was already suggested by Gadamer (*l.c.*) ; like berberine (I) forms characteristic addition compounds with chloroform (greyish-yellow crystals, m.p. 189°) and with acetone (red-brown crystals, m.p. 143°).

Jatrorrhizine (II)-iodide, $C_{20}H_{20}O_4NI+H_2O$, m.p. 210°–211°, crystallises in reddish-yellow needles. (II)·Cl yellow (from H_2O) or copper coloured needles (from EtOH), both forms melting at 206° ; (II)·NO_3 glistening, golden-yellow needles, m.p. 225°. On reduction of (II) rac. (V) (m.p. 216°–217°, from alcohol) is obtained.

Columbamine (III), $C_{20}H_{20}O_4N \cdot OH$, has only been isolated as the rac. *tetrahydro-derivative* (VI), m.p. 223°–224° (from MeOH) (*cf.* Späth and Burger, *l.c.*).

For the absorption spectra of the three alkaloids, *see* Feist, Awe, and Etzrodt (*l.c.*).

Späth and Polgar (Monatsh. 1929, **52**, 117) isolated (I), (II), and (III) from *Berberis vulgaris*. Gadamer, Späth, and Mosettig (Arch. Pharm. 1927, **265**, 675) found *d*-(VI) in *Corydalis cava*. (II) was further isolated from *Mahonia philippensis* (Castro, Santos, and Valenzuela, 1933, A., 878), (II) and (III) from *Arcangelisia flava* (Santos, 1932, A., 664), and *Berberis Thunbergii* D.C. var. *Maximowiczi*, Franch. (Kondo and Tomita, 1931, A., 242).

Constitutions.—The constitution of (I) has been proved by Feist and Sandstede (*l.c.*) who by

permanganate oxidation obtained corydaldine (right part of the molecule) and *o* hemipinic acid (left part of the molecule). Gadamer's suggestions (*l c.*) concerning the relationship between (I) and berberine is now certain, (I) is a base with two MeO-groups instead of a methylenedioxy-group in the 2 3-position of berberine. (II) (Spath and Bohm, Ber. 1922, **55**, 2985) and (III) (Spath and Burger, *l c.*) were methylated at the phenolic OH group and thus converted into (I). By careful oxidation of (V) ethyl ether with permanganate Späth and Duschinsky (*l.c.*) obtained the methyl ethyl ether of nor *m* hemipinic acid and 7-methoxy 6 ethoxy-1-keto-1 2 3 4 tetrahydro*iso*quinoline, which was conclusive proof that the phenolic OH group was in position 3. A similar oxidation of (VI)-ethyl ether (Späth and Burger, *l c*) showed the phenolic OH-group of (III) to be in position 2.

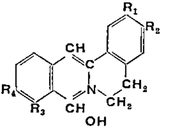
Syntheses.—Unsuccessful attempts at syntheses of the tetrahydropalmatine skeleton were reported by Pictet and Malinovski (Ber. 1913, **46**, 2688) and by Pictet and Chou (Ber 1916, **49**, 370). Späth and Lang (Ber. 1921, **54**, [B], 3064), starting from tetrahydroberberine, removed the methylenedioxy group with alcoholic potash and methylated the phenolic base with dimethyl sulphate. The quaternary methosulphate was converted into (IV) (m p 146°–147°, no depression with the natural product), and finally into (I) I (m p 240°) by oxidation with iodine solution The yields are poor. A second synthesis of (I), starting from quaternary berberine sulphate and removing the methylenedioxy-group with phloroglucinol H_2SO_4 has been reported by Spath and Quietensky (Ber. 1925, **58**, [B], 2267) The phenolic base is methylated with dimethylsulphate, the yields are good

Interesting syntheses of (IV) and of the iodide of (I) have been reported by Haworth, Koepfli, and Perkin (J C S 1927, 548) ; a further synthesis of the latter is due to Oberlin (Arch Pharm. 1927, **265**, 271), and Osada obtained (IV) starting with protopine (Amer Chem Abstr 1928, **22**, 592).

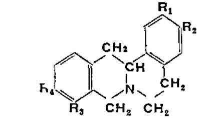
Spath and Quietensky (*l.c*) methylated with small amounts of dimethyl sulphate the phenolic base obtained in their second synthesis (*see above*), and obtained a compound which after reduction yielded (V).

In a second synthesis, starting from *r*- and *d* tetrahydroberberine Spath and Mosettig (Ber 1927, **60**, 383) obtained the *r*- and *d* forms of (IV), (V), and (VI). *d* (V) (m p 237°–238°) is identical with corypalmine.

The following are the structural relations of the Calumba alkaloids :



(I) $R_1=R_2=R_3=R_4=OMe$
(II) $R_1=R_3=R_4=OMe$, $R_2=OH$
(III) $R_2=R_3=R_4=OMe$; $R_1=OH$



(IV) $R_1=R_2=R_3=R_4=OMe$
(V) $R_1=R_3=R_4=OMe$; $R_2=OH$
(VI) $R_2=R_3=R_4=OMe$; $R_1=OH$

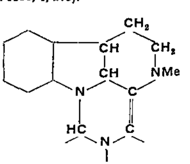
Schl

CALYCANTHINE (I) and *iso*-**CALYCANTHINE** (II) are two alkaloids occurring in two *Calycanthus* species (*floridus*, *glaucus*) and in *Meratia præcox* (Fam. Calycanthaceæ) (I) was first isolated by Eccles (Proc. Amer. Pharm. Assoc. 1888, **84**, 382); the first chemical investigation was undertaken by Gordin (J Amer. Chem. Soc. 1905, **27**, 144).

Extraction (cf. Gordin, 1905, l c , and Manske, J. Amer. Chem. Soc. 1929, **51**, 1836) : the seeds are first defatted by extraction with light petroleum, etc The alkaloid is then obtained by extraction with hot EtOH. After evaporation the residue is taken up in dilute HCl. The dark brown solution is carefully basified when the crude crystalline base separates and is recrystallised from dilute EtOH or dilute acetone (yield approximately 1 7–2 5%)

Calycanthine (I), $C_{22}H_{28}N_4$ (Spath and Stroh, Ber. 1925, **58**, [B], 2131) or $C_{22}H_{26}N_4$ (Manske, *l c.* 1929), m.p. 216°–218° or 245° (dry), $[\alpha]_D^{18}$ +684 3°, crystallises with 1 mol. of H_2O in orthorhombic bipyramids, it is readily soluble in Et_2O and $CHCl_3$, sparingly soluble in H_2O, reacts alkaline to litmus and has a bitter taste. It probably contains two secondary and two tertiary N atoms. For colour reactions *cf.* Gordin (*l.c.*). The salts of (I) are mostly crystalline, $B{\cdot}2HNO_3$, prisms, m.p. 208°–209° (from dilute HNO_3) ; $B{\cdot}2H_2SO_4$, silky needles, m.p. 184° (dry) ; $B{\cdot}H_2SO_4$, m.p. 229° (dry) , chloroaurate, m.p. 196° (dry) ; picrate, m p. 185°, yellow silky needles, sparingly soluble H_2O and EtOH ; *cf.* Gordin (J. Amer. Chem Soc. 1905, **27**, 1418).

By interaction of HNO_2 and (I) a dinitrosamine was obtained (Gordin, *l c*), a Zerewitinoff estimation (Späth and Stroh, *l c*) demonstrated two active H-atoms (two N-H groups) ; these findings are difficult to correlate with a partial formula for (I), drawn from Manske's degradation experiments (Canad. J Res. 1931, **4**, 275).



iso-**Calycanthine** (II).—Gordin (J. Amer. Chem. Soc. 1909, 31, 1305) reported the isolation of a second alkaloid (II) from *C. glaucus*. Although there is no reason for questioning the existence of (II), Gordin's first starting material, from which he isolated (I), must have been *C. floridus*, (I) and (II) have never been found together, (I) is obtained from *C. floridus* and *Meratia præcox*, and (II) from *C. fertilis* (*C. glaucus*).

(II) forms thick prisms, melting at 235°–236°, $[\alpha]_D^{22}$ +697·9°, soluble in acetone, $CHCl_3$, and hot EtOH, sparingly soluble in Et_2O, cold EtOH, or benzene. The salts are mostly crystalline.

(I) and (II) are very toxic ; 10 mg. produce strychnine-like convulsions in a frog, lethal dose for rabbits 20 mg. per kg. body weight, death from paralysis of respiration (*cf.* Cushny, Arch. intern. de pharmac. et de thérapie, 15, 487). From the leaves of *C. floridus*, Mirande (Compt. rend. 1912, 155, 783) has isolated small amounts of prussic acid ; Scalione (Ind. Eng. Chem. 1916, 8, 729) has found trimethylamine in the leaves of *C. occidentalis*. For constituents of the volatile oil of *C. floridus*, *see* Miller, Taylor and Eskew (J. Amer. Chem. Soc. 1914, 36, 2182). Schl.

CAMBOGIA or GAMBOGE. An orange red gum resin obtained from *Garcinia Hanburyi*, Hook (Fam. Guttiferæ) growing in Camboja, Siam and Cochin China. Indian gamboge is obtained from *G. morella* Desrouss. Used as a purgative and also as a pigment.

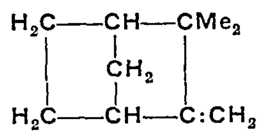
CAMELINE OIL, DODDER OIL, or GERMAN SESAME OIL, is obtained from the seeds of *Camelina sativa* L. Fr. (Fam. Cruciferæ). Several centuries ago the cultivation of cameline was of considerable importance in Germany, but it is now only grown on a small scale in Central Europe and Russia. The seed contains 30–40% of oil, which is golden-yellow in colour and has a pungent taste and smell. It is a semi-drying oil, on exposure to air it dries slowly and on boiling with litharge or manganese salts it yields a slowly drying varnish. The cold-pressed oil is used for edible purposes in Russia ; the hot-pressed grades are used for soap-making on the Continent.

The properties of the oil are as follows : d^{15}, 0·920–0·927 ; f.p. −15° to −19°C. ; saponification value 185–188 ; iodine value 133–154 (the higher iodine values are found for oils from colder regions, *e.g.* North Russia, *cf.* Ivanow, Chem. Umschau, 1930, 37, 349 ; Boekenoogen, Fettchem. Umschau, 1933, 40, 55 ; Heller, Angew. Chem. 1933, 46, 441) ; unsaponifiable matter 1·16% (one sample, Grimme, Chem. Rev. 1912, 19, 102) ; m.p. of fatty acids, 18°–20°C., mean molecular weight of fatty acids, 296·3. The latter figure and low saponification value of the oil suggest that the oil may contain erucic acid. The presence of small amounts of this acid, and of linolenic acid, together with oleic, linolic, and saturated acids (about 10% ?) in cameline oil is reported by Boekenoogen (private communication). J. L. and E. L.

CAMPEACHY WOOD. Logwood.

CAMPHANIC ACID. The lactone of hydroxy-camphoric acid (*v.* Camphor).

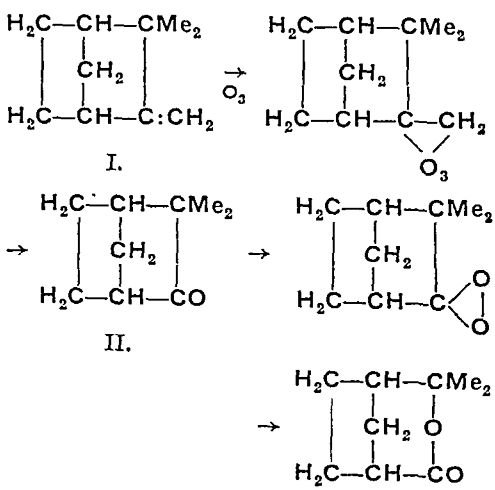
CAMPHENE.



The dicyclic hydrocarbon, *camphene*, $C_{10}H_{16}$, is crystalline, and it has therefore been obtained pure and free from isomerides. It occurs fairly widely distributed in nature both in the optically active and inactive forms. *l*-Camphene is probably most conveniently obtained from the oil of *Abies Sibirica*. The optically active and inactive forms have approximately the same melting-points and the following constants have been recorded : m.p. 51°–52°, b.p. 158·15°–158·5°/760 mm., d_4^{54} 0·84224, n_D^{54} 1·5514, $[\alpha]_D$ +103·89°, −85·9° (in ether). The hydrocarbon can be identified by its melting-point, by its conversion with the Bertram-Walbaum reagent into *iso*borneol, and by its oxidation in acetic acid solution to camphenilone.

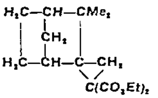
Camphene was prepared in the laboratory prior to its isolation from natural sources. It is formed when hydrogen chloride is removed from bornyl or *iso*bornyl chlorides, this reaction having been investigated as far back as 1831 by Oppermann (Pogg. Ann. 1831, 22, 193). The most suitable conditions for the conversion of bornyl chloride into camphene have been carefully studied in view of its importance as a stage in the manufacture of " synthetic " camphor.

Owing to the facility with which camphene undergoes molecular rearrangements and the somewhat abnormal results obtained on oxidation with potassium permanganate in alkaline solution, the determination of the structure of camphene has afforded considerable difficulty. The constitution (I) now assigned to it was first suggested by Wagner (J. Russ. Phys. Chem. Soc. 1899, 31, 680) and proof is furnished by the following facts : (i) on ozonolysis it yields formaldehyde, *camphenilone* (II), and the *lactone* (III), the latter being a secondary product formed by the reactions indicated below (Harries and Palmén, Ber. 1910, 43, 1432) :



I. II. III.

and (ii) by the oxidation of the condensation product (IV) of camphene with ethyl diazoacetate to *cyclo*propane-1:1:2 tricarboxylic acid (V) which establishes the exocyclic ethylenic linkage.



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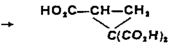
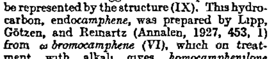
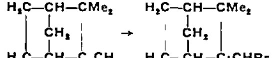


V.

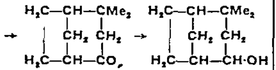
Whilst the oxidation of camphene with potassium permanganate in acetic acid yields cam phenilone (II), in alkaline solution the dibasic acid, *camphenic acid* (X) is obtained, the formation of which suggests that camphene should be represented by the structure (IX). This hydrocarbon, endo*camphene*, was prepared by Lipp, Götzen, and Reinartz (Annalen, 1927, 453, 1) from ω *bromocamphene* (VI), which on treatment with alkali gives *homocamphenilone* (VII). Reduction of the ketone with sodium and alcohol yields the alcohol *homocamphenilol* (VIII), from which by dehydration endocamphene is obtained.



I. VI.

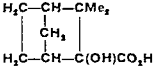


VII. VIII.

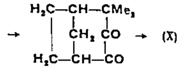


IX. X.

The oxidation of camphene to camphenic acid, which occurs only in the presence of alkali (Langlois, Ann. Chim. 1919, [ix], 12, 301), is due to the rearrangement of the primary oxidation product, *camphenylic acid* (XI) into *carbocamphenilone* (XII), which is then further oxidised to camphenic acid.

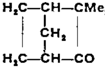


XI.



XII.

Camphene has been prepared synthetically by the action of magnesium methyl iodide on camphenilone (II), the tertiary alcohol, *methyl camphenilol* or *camphene hydrate* (XIII), giving on dehydration camphene (I).



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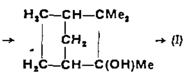
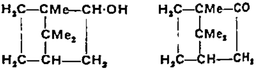


XIII.

Other methods for the preparation of camphene are (i) the dehydration of borneol and *iso*borneol, (ii) the action of acetic anhydride on bornylamine.

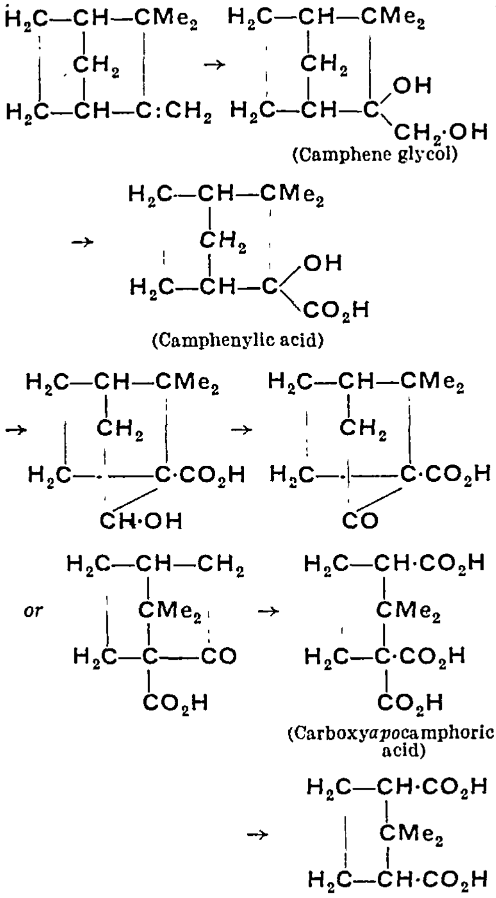
On oxidation with chromic acid camphene yields *camphor* (XV) (Armstrong and Tilden, Ber. 1879, 12, 1756; Kachler and Spitzer, Annalen, 1880, 200, 359). This reaction involves a Wagner Meerwein rearrangement and it is possible that camphene hydrate (XIII) is first formed, which tautomerises to *borneol* (or *isoborneol*) (XIV), the latter then being oxidised to camphor.



XIV. XV.

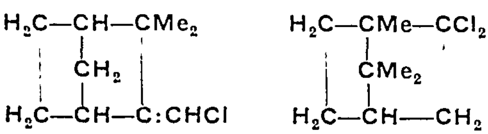
This method has been used for the manufacture of "synthetic" camphor; for fuller particulars see CAMPHOR, SYNTHETIC, p. 249.

The oxidation of camphene with nitric acid has been studied by Riban (Ber. 1878, 11, 391), Armstrong and Tilden (*ibid.* 1879, 12, 1756), Marsh and Gardner (J.C.S. 1891, 59, 648), and by Komppa (Ber. 1901, 34, 2472; 1908, 41, 2747; 1911, 44, 863, 1536; Annalen, 1909, 366, 71; 368, 126), and it has been shown to proceed in accordance with the following scheme:

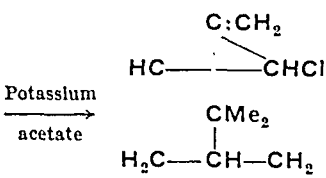


(Camphene glycol) (Camphenylic acid) (Carboxy*apo*camphoric acid) (*apo*Camphoric acid)

ω-*Chlorocamphene* (XVI), b.p. 95°–98°/15 mm., has been prepared by Langlois (Ann. Chim. 1919, [ix], 12, 193) by the action of chlorine on camphene, whilst two stereoisomeric *a-chlorocamphenes* (XVII), m.p. 20°, b.p. 193°–197°, and m.p. 123°–129°, b.p. 194°–200°, have been obtained by Meerwein and Wortmann (Annalen, 1923, 435, 194) from *a-dichlorocamphane* (XVIII) prepared by the action of phosphorus pentachloride on camphor.



XVI. XVIII.

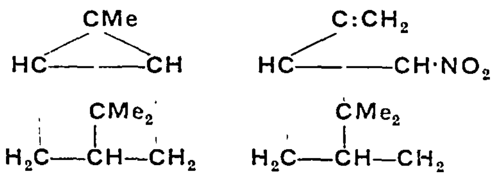


XVII.

ω-*Bromocamphene*, which is an oil, was first prepared by Wallach (Annalen, 1885, 230, 235) by the bromination of camphene. Its reactions have been studied by Langlois (*l.c.*) and also by Lipp and his collaborators (J. pr. Chem. 1922, [ii], **105**, 50 ; Annalen, 1927, **453**, 1).

As was first observed by Berthelot (Annalen, 1859, **110**, **367**) camphene on treatment with hydrogen chloride yields *iso*bornyl chloride. This important reaction has since been studied in great detail and the experiments of Aschan (Annalen, 1911, **383**, 7) and more especially of Meerwein and Emster (Ber. 1920, **53**, [B], 1815 ; 1922, **55**, [B], 2500) have shown that a mixture of *iso*bornyl chloride and *camphene hydrochloride*, m.p. 125°–127°, is formed, when camphene is treated with hydrogen chloride in methyl alcoholic or ethereal solution. The latter hydrochloride which is extremely unstable, is tautomeric with bornyl and *iso*bornyl chlorides. The percentage of camphene hydrochloride in the mixture can be readily estimated by taking advantage of the fact that it can be titrated like free hydrochloric acid.

ω-*Nitrocamphene*, *l*-, m.p. 84°–85°, *dl*-, m.p. 64°, known also as *camphenilic nitrite*, can be readily prepared by the action of oxides of nitrogen on camphene (Jagelki, Ber. 1899, **32**, 1498 ; Lipp, Annalen, 1911, **382**, 291 ; 1913, **399**, 241 ; 1914, **402**, 343 ; Blaise and Blanc, Comp. rend. 1899, **139**, 886 ; Bull Soc. chim. 1900, [iii], **23**, 164). It yields on treatment with alkali camphenilone. Two further nitro-camphenes have been prepared (Forster, J.C.S. 1899, **75**, 1144 ; Nametkin and Zabroda, Annalen, 1925, **441**, 181). The second of these, b.p. 119°–119·5°, prepared by the action of nitric acid on *tricyclene* (XIX) is probably represented by (XX), but the constitution of Forster's *nitrocamphene*, m.p. 56°, obtained by the action of silver nitrate on 2-bromo-2-nitrocamphane is not known.

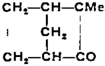


XIX. XX.

The hydration of camphene with acetic–sulphuric acid mixture (Bertram and Walbaum, J. pr. Chem. 1894, [ii], **49**, 8) yields mainly *iso*borneol with some borneol. This is the normal product of the hydration and it occurs with the majority of hydrating reagents. Since it forms an intermediate stage in the manufacture of "synthetic" camphor the reaction has been studied in great detail and it forms the subject of numerous patents. If, however, camphene is hydrated in ethereal solution with Aschan's reagent " diethyl oxonium sulphate " (prepared by treating ether with monohydrate) it yields *camphene hydrate*, m.p. 150°–151° ; *phenylurethane*, m.p. 89° (Aschan, Medd. K. Vetenskapsakad. Nobel-Inst. 1919, **5**, No. 8, 19). This alcohol is obtained also by the action of milk of lime on either bornyl chloride or camphene hydrochloride (Aschan, Ber. 1908, **41**, 1092). A stereoisomeric *alcohol*, m.p. 117°–118° ; *phenylurethane*, m.p. 126°, was prepared by Moycho

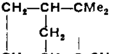
and Zienkowski (Annalen, 1905, **340**, 58) by the action of magnesium methyl iodide on camphenilone. As has been shown by Meerwein and his collaborators (Annalen, 1923, **435**, 174; 1927, **453**, 16) borneol, *iso*borneol, and camphene hydrate, like the related chlorides, are tautomerides. J. L. S.

CAMPHENILONE.

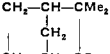


The ketone *camphenilone*, $C_9H_{14}O$, does not occur in nature. *dl* Camphenilone has m p. 38°, b.p. 195°, d^{38} 0 9705, n_D 1·469, *semicarbazone*, m.p 224°, *oxime*, m p. 41°–42°. Both optically active modifications have been prepared; *d*-, m p. 41°–42°, $[a]_D^{18\ 5}$ +30 05 (in alcohol), *l*, m.p. 39°, b p. 193°/760 mm., $[a]_D$ −60 8° (in benzene) (Aschan, Annalen, 1915, **410**, 223, Huckel and Tappe, Ber. 1936, **69**, B, 2770)

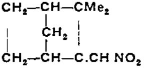
The ketone (I) can be prepared by the oxidation of camphene (II) (Blaise and Blanc, Bull Soc chim. 1900, [iii], **23**, 173) or by the oxidation of ω *nitrocamphene* (III) with potassium per manganate (Jagelki, Ber 1899, **32**, 1498, Komppa and Hintikka, Annalen, 1912, **387**, 294).



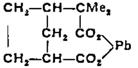
II.



I.



III.



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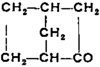
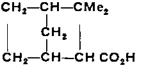


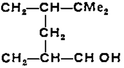
V.



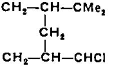
VI.

The ketone has been synthesised by G. Komppa and Hintikka (Ber. 1914, **47**, 1550) by the distillation of the lead salt of camphenic acid (IV), by Diels and Alder (Annalen, 1926, **470**, 63; 1931, **486**, 202) by the methylation of norcamphor (V) and by G. Komppa and O Komppa (Ber. 1936, **69**, 2606) from *iso*camphenilanic acid (VI) through camphenylamine and camphenilol.

On reduction camphenilone yields the secondary alcohol, *camphenilol* (VII). Two stereoisomeric *dl* forms of this alcohol have been described, m.p. 91·5°–92° and 74°–75° respectively (G. Komppa and Beckmann, Annalen, 1936, **522**, 137), the related optically active isomerides have m p. 76°, $[a]_D$ −23 0°, and m p. 98°–101°, $[a]_D$ +33 3°. They were prepared from *l* camphene (Huckel and Tappe, Ber. 1936, **69**, [B], 2770).



VII.



VIII.

By the action of phosphorus pentachloride on the alcohol *camphenilyl chloride* (VIII), m p. 54°, b.p 70°–76°/15 mm., is obtained, which is, however, not homogeneous

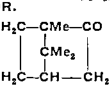
The dehydration of camphenilol or the removal of hydrogen chloride from camphenilyl chloride yields a complex mixture of hydrocarbons, in which santene predominates, *apocyclene* and *apo*bornylene being formed also (Hintikka and Komppa, Bull. Soc. chim. 1917, [iv], **21**, 14, Snitter, Bull. Inst Pin, 1933, **178**, 200; Gratton and Simonsen, J C S. 1935, 1621; Komppa and Beckmann, Annalen, 1936, **522**, 137; Lipp and Daniels, Ber. 1936, **69**, [B], 1813, 2251). J. L. S.

CAMPHENOL *v.* CARVENONE.

CAMPHOCHOL. A molecular compound of camphor and apocholic acid (Rheinboldt *et al.* Z. physiol Chem. 1929, **184**, 219)

CAMPHOL. A name for synthetic borneol (Berthelot, Ann Chim. 1859, [iii], **56**, 51).

CAMPHOR.



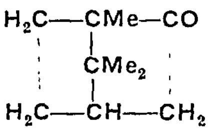
The dicyclic ketone *camphor*, $C_{10}H_{16}O$, does not occur very widely distributed in nature. *d*-Camphor occurs in the tree *Cinnamomum camphora* Nees and this forms the main source of the natural ketone. Camphor occurs in all parts of the tree, but mainly in the trunk. The most extensive forests of *C. camphora* are found in Formosa, where the production of camphor is a government monopoly; the tree has, however, been cultivated in various other tropical and semi tropical countries. No large industry has, however, been developed. *l*-Camphor is found in the oil from *Blumea balsamifera* and in that from *Artemisia tridentata typica* (Adams and Oakberg, J. Amer. Chem. Soc. 1934, **56**, 457), and *dl*-camphor in the oil from *Chrysanthemum sinense*, var. *japonica*.

Camphor has a characteristic odour, crystallises in thin plates, and sublimes readily at room temperature. The *d*- and *l*- forms of camphor melt at 178 5°–179°, $[a]_D$ ±44·22° (in alcohol, c=20), the rotatory power varies very greatly with the nature of the solvent and the concentration. *dl*-Camphor has m p. 178°–178 5°, b.p. 209°/759 mm., d_0^0 1 000. Camphor can be

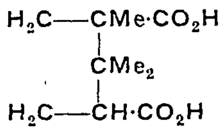
identified by the preparation of the *oxime*, m.p. 119·5° or the *semicarbazone*, m.p. 245°. The *d*-, *l*-, and *dl*-forms of camphor, and also their derivatives, differ as a rule little in melting-points, one notable exception being the *phenylsemicarbazones*, where the *d*- and *l*-forms have m.p. 153°–154°, and the *dl*-, m.p. 171·5°–172·5°. In the absence of other carbonyl derivatives camphor can be estimated quantitatively by the preparation of its sparingly soluble 2:4-*dinitrophenylhydrazone*, m.p. 175°.

Frequent mention of camphor, which early found employment in medicine, is found in alchemical literature. Its composition and molecular weight were first correctly determined by Dumas (Annalen, 1833, **6**, 245), and since that time no natural substance has formed the subject of such intensive study. (For an account of early work on camphor, *see* Aschan, "Die Constitution des Camphers und seiner wichtigsten Derivative," Braunschweig, 1903).

Camphor on oxidation gives a dibasic acid, *camphoric acid*, $C_{10}H_{16}O_4$, and the structure (I) now accepted for camphor is based upon that suggested for camphoric acid (II) by Bredt in 1893.

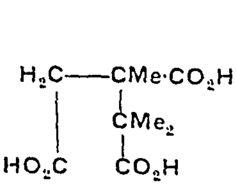


I.

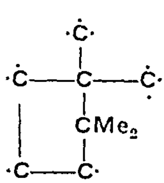


II.

Camphoric acid can exist in *cis*- and *trans-forms. It is only the cis- form, which has the* carboxyl groups on the same side of the plane of the ring, that is related to camphor. The more important evidence in support of the formulæ suggested for these two substances may be briefly summarised under the following heads: (i) both camphor and camphoric acid are saturated substances, and they must therefore be dicyclic and monocylic respectively; (ii) camphor and camphoric acid are optically active and they must therefore contain at least one centre of asymmetry; (iii) camphor is a ketone, since it forms an oxime and can be reduced to a secondary alcohol; (iv) camphor must contain the grouping $—CO—CH_2—$ since it gives an hydroxymethylene derivative and yields on oxidation a dibasic acid, camphoric acid, in which the two carboxyl groups are not similarly situated; (v) oxidation of camphor or of camphoric acid with nitric acid gives *camphoronic acid*, $C_9H_{14}O_6$, shown by Perkin and Thorpe's synthesis (J.C.S. 1897, **71**, 1189) to be represented by (III). From this it follows that camphor and camphoric acid must contain



III.



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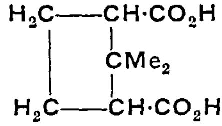
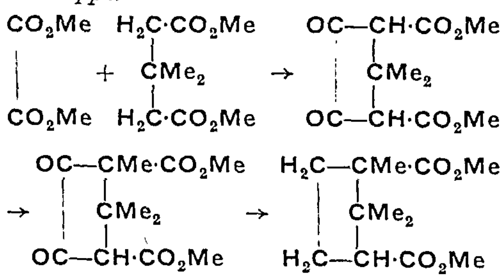


V.

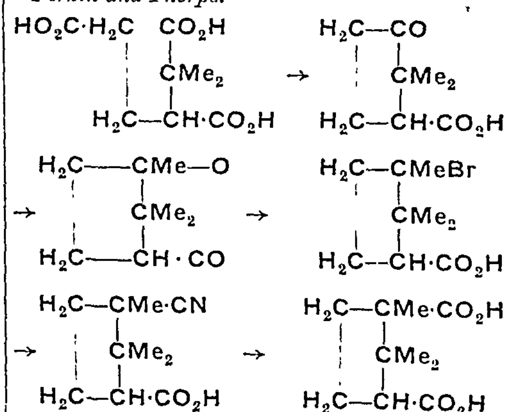
the carbon skeleton (IV); (vi) the sodium derivative of camphor gives with cyanogen, *cyanocamphor*, $C_{10}H_{15}O·CN$, yielding on hydrolysis *homocamphoric acid*, $C_9H_{16}(CO_2H)_2$. This acid must be a derivative of either glutaric or adipic acid, since distillation of its calcium salt gives the ketone camphor; (vii) direct proof of the presence of the *cyclo*pentane ring is furnished by the oxidation of bornyl chloride to apo*camphoric acid* (V) synthesised by Komppa (Ber. 1901, **34**, 2472).

The reactions outlined above can be explained readily on the Bredt formulæ (I) and (II), and the structure for camphoric acid has been confirmed by its synthesis practically simultaneously by Komppa (Ber. 1903, **36**, 4332; Annalen, 1909, **370**, 225) and by Perkin and Thorpe (J.C.S. 1904, **85**, 146; 1906, **89**, 799). These two syntheses are outlined in the schemes set out below:

Komppa.



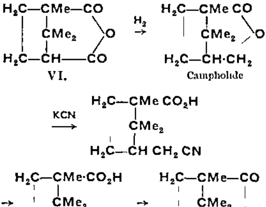
Perkin and Thorpe.



The camphoric acid so obtained was optically inactive, but it was readily resolved into the two enantiomorphs, *d*- and *l*-camphoric acids, identical with those obtained by the oxidation of *d*- and *l*-camphor.

As mentioned above, camphor can be prepared by the distillation of the calcium salt of *homocamphoric acid* (VII), obtained from *camphoric anhydride* (VI) by the reactions given

below, first carried out by Haller (Compt. rend 1889, **109**, 68, 112 ; 1896, **122**, 440).



VI. Campholide VII.

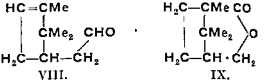
Although camphor has two centres of asymmetry, as was first pointed out by Aschan (Annalen, 1901, **316**, 212), both these are occasioned by the carbonyl group, and camphor can therefore only give two optically active forms. This is confirmed by the fact that the saturated hydrocarbon, camphane, derived from camphor, is optically inactive

Camphor is of very great technical importance, being used largely, *inter alia*, in the manufacture of celluloid, plastics, smokeless powders, and medicinal products Since the natural product is limited in quantity camphor is now manufactured on a considerable scale from pinene The subject of the manufacture of "synthetic" camphor is dealt with elsewhere One of the main processes involves the following series of reactions .

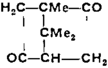
Pinene → Bornyl chloride → Camphene → *iso*Borneol → Camphor

On reduction camphor gives the secondary alcohols borneol and *iso*borneol With a platinum black catalyst Vavon and Peignier (Compt. rend 1925, **181**, 184) found the product to be nearly pure *iso*borneol, prolonged treatment giving camphane With a nickel oxide catalyst at 320°–350°, using high pressures, a mixture of borneol and *iso*borneol results, whilst with an alumina nickel oxide catalyst these alcohols are accompanied by *iso*camphane (Ipatiev, Ber. 1912, **45**, 3206). The hydrocarbon is evidently formed by the dehydration of the alcohols to camphene followed by hydrogenation.

Camphor is fairly resistant to the action of oxidising agents. In alcoholic solution it is oxidised by the air in sunlight to *a campholenaldehyde* (VIII) and other substances (Ciamician and Silber, Ber. 1910, 43, 1341). With Caro's reagent *a campholide* (IX) and a lactone, $C_{10}H_{16}O_4$, is obtained (Baeyer and Villiger, Ber. 1899, **32**, 3625 ; Locquin, Compt. rend. 1911, **153**, 284). In the presence of mineral acids chromic acid oxidises camphor to *camphoronic and iso-camphoronic acids* (Kachler,



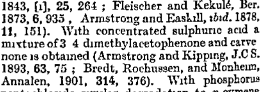
VIII. IX.



X.

Ber 1880, **13**, 487), but in their absence the diketone p *diketocamphane* (X) is obtained (Bredt, J. pr. Chem. 1923, [ii], **106**, 336). With potassium permanganate in alkaline solution or with potassium ferricyanide camphoric acid results and this acid, together with camphoronic, *iso*camphoronic, trimethyl- and dimethyl-succinic acids, is obtained by the action of nitric acid (Grosser, Ber. 1881, **14**, 2507 ; Étard, Compt. rend. 1900, **130**, 570 ; Bredt, Ber. 1893, **26**, 3047)

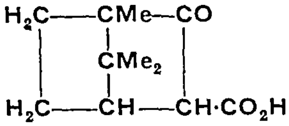
The action of dehydrating agents on camphor results as a rule in the formation of monocyclic derivatives, ring fission occurring generally between the 1 and 7 carbon atoms of the camphor molecule. Thus with phosphorus pentoxide camphor yields *p* cymene (Dumas and Péligot, Compt. rend. 1836, **4**, 406 ; Kekulé and Pott, Ber 1869, **2**, 121 ; Armstrong and Miller, *ibid*. 1883, **16**, 2259). With zinc chloride *p cymene, 1 2 dimethyl 4-ethylbenzene* and 1 2 3 5-tetramethylbenzene and carvacrol are produced (Armstrong and Miller), whilst the phenol is formed also by the action of iodine (Claus, Annalen, 1842, **44**, 301 ; J. pr. Chem. 1843, [i], **25**, 264 ; Fleischer and Kekulé, Ber. 1873, **6**, 935 , Armstrong and Easkill, *ibid*. 1878, **11**, 151). With concentrated sulphuric acid a mixture of 3 4 dimethylacetophenone and carvenone is obtained (Armstrong and Kipping, J.C S. 1893, **63**, 75 ; Bredt, Rochussen, and Monheim, Annalen, 1901, **314**, 376). With phosphorus pentachloride similar degradation to *p* cymene and carvacrol may occur, but Meerwein and Wortmann (Annalen, 1923, **436**, 190) have shown that under suitable conditions *a camphor dichloride, 2.2′-dichlorocamphane*, m p. 146°–148°, (XI) is obtained, which in the presence of stannous chloride in toluene solution isomerises to 2:10 *dichlorocamphane*, m.p. 178°–179° (XII).



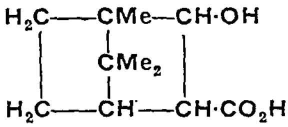
XI. XII.

Camphor reacts readily with sodium or sodamide to give *sodiocamphor* (Bruhl, Ber. 1903, **36**, 1305 ; 1904, **37**, 2171), some reduction to borneol and *iso*borneol occurring during its formation. *Sodiocamphor reacts with carbon dioxide to give*

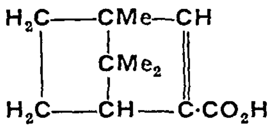
camphor-carboxylic acid [XIII], m.p. 127°–128°, $[\alpha]_D \pm 18°$ (Baubigny, Ann. Chim. 1870, [iv], **19**, 221; Bredt and Sandkuhl, Annalen, 1909, **369**, 11). The acid is formed also from α-bromocamphor by the Grignard reaction (Zelinski, Ber. 1903, **36** 308 ; Brühl, ibid. 688 ; Malmgren, ibid. 2622). When reduced electrolytically (Bredt, Scheen, and Quaritsch, Annalen, 1906, **348**, 199 ; Bredt and Sandkuhl, *ibid.* 1909, **366**, 16 ; J. pr. Chem. 1922, [ii], **104**, 1 ; Bredt, Drouven, Schumann, and Scholl, *ibid.* 1931, [ii], **131**, 132) it yields a mixture of cis- and trans-*borneolcarboxylic acids* (XIV), *cis-*, m.p. 101°–102° (*dl-*, m.p. 129°–130°) ; *trans-*, m.p. 171° (*dl-*, m.p. 144°–145°), which both give on dehydration *bornylenecarboxylic acid* (XV). The hydroxy-acids are highly



XIII.

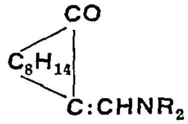


XIV.

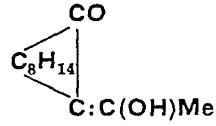


XV.

reactive and undergo a number of interesting molecular rearrangements. *Cyanocamphor*, m.p. 127°–128°, $[\alpha]_D +12{\cdot}16°$, was prepared by Haller (Compt. rend. 1878, **87**, 843) by the action of cyanogen or cyanogen chloride on sodiocamphor. It can be prepared also more conveniently by the action of hydroxylamine on hydroxymethylenecamphor (Bishop, Claisen, and Sinclair, Annalen, 1894, **281**, 349). It yields homocamphoric acid on prolonged hydrolysis with alkali. Alkyl derivatives of camphor, *α-methylcamphor*, m.p. 38°, $[\alpha]_D +30°$, are prepared by the action of alkyl halides on sodiocamphor or by heating the alkyl camphorcarboxylic acids; dialkyl derivatives have also been described (Haller and Bauer, Ann. Chim. 1917, [ix], **8**, 117 ; Haller and Louvrier, *ibid.* 1918, [ix], **9**, 190). By the action of amyl formate on sodiocamphor, Bishop, Claisen, and Sinclair (Annalen, 1894, **281**, 330), prepared *hydroxymethylenecamphor*, m.p. 81°. The structure of this substance has been discussed by Pope and Read (J.C.S. 1909, **95**, 175), and by Singh and Bhaduri (J. Indian Chem. Soc. 1930, **7**, 771). It condenses readily with bases to give products of the general formula (XVI) from which the base can be regenerated by the action of bromine (Pope and Read, J.C.S. 1912, **101**, 2337 ; 1913, **103**, 444). By the action of acetyl chloride or



XVI.

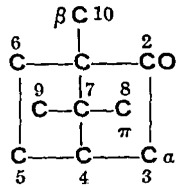


XVII.

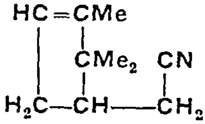
acetic anhydride on sodiocamphor, *acetylcamphor*, b.p. 118°–118·5°/11·2 mm., has been prepared which probably consists mainly of the enolic form (XVII). *Benzoylcamphor* has been obtained in both enolic and ketonic forms (Forster, J.C.S. 1901, **79**, 991 ; 1903, **83**, 98). These mutarotate in solution, enolic form m.p. 89·5°, $[\alpha]_D+331°$, ke to form m.p. 112°, $[\alpha]_D+152°$, a final value $[\alpha]_D+258°$, in alcohol (Lowry, MacConkey, and Burgess, *ibid.* 1928, 1333).

Derivatives of Camphor.

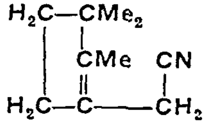
System of numbering :



Camphoroxime, *d-* and *l-*, m.p. 119°, $[\alpha]_D$ −42·40°, +41·7°; *dl-*, m.p. 118°, is most readily prepared by the method of Auwers (Ber. 1899, **22**, 605). It can be hydrolysed to camphor with formaldehyde and hydrochloric acid (Lapworth, J.C.S. 1907, **91**, 1132). When reduced with sodium and alcohol a mixture of *bornylamine*, m.p. 163°, $[\alpha]_D$ +45·5°, and neo*bornylamine*, m.p. 183°, $[\alpha]_D$ −43·7°, is obtained (Leuckart and Bach, Ber. 1887, **20**, 111 ; Forster, J.C.S. 1898, **73**, 370 ; Konovalov, J. Russ. Phys. Chem. 1901, **33**, 46). When camphoroxime is digested with mineral acids or acid chlorides it undergoes the Beckmann rearrangement and gives a mixture of α-campholenonitrile, α-campholenoamide, α-campholenic acid, β-campholenonitrile, β-campholenoamide, β-campholenic acid, and dihydro-β-campholenolactone, depending upon the conditions used (Naegeli, Ber. 1884, **17**, 805 ; Goldschmidt and Schmidt, *ibid.* 2071 ; Tiemann, *ibid.* 1896, **29**, 3007 ; 1897, **30**, 243, 328 ; Béhal, Bull. Soc. chim. 1895, **13**, 837 ; Konovalov, J. Russ. Phys. Chem. 1901, **33**, 46). The primary product of the reaction is *α-campholenonitrile* (I), b.p. 226°–227°, $[\alpha]_D$ +7·3°, which can be hydrolysed through the *amide*, m.p. 130·5°, $[\alpha]_D$ −4·9°, to the *acid*, b.p. 142°–144°/10 mm., $[\alpha]_D$ +9·37°. α-Campholenonitrile readily isomerises when heated with mineral acids to *β-campholenonitrile* (II), b.p. 225° *amide*, m.p. 86°, *acid*, m.p. 52°. Both acids lose carbon dioxide when heated to give the hydrocarbon, *campholene* (III), b.p. 134°/758 mm., $d^{20°}$ 0·8039, n_D 1·4466.



I.



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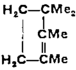
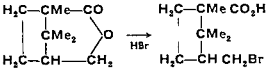


III.

The structures of these acids have been proved by their degradation (Tiemann, Ber. 1895, 28, 2170; 1896, 29, 529, 3014, 3023; 1897, 30, 405).

When camphor is fused with alkali it gives a mixture of *campholic* acid, *d*- and *l*-, m.p. 106°–107°, *dl*-, m.p. 109°, and *isocampholic* acid, the latter being difficult to purify (Delalande, Ann. Chim. 1841, [iii], 1, 120). Campholic acid must be represented by (IV) since it has been prepared by Haller and Blanc (Compt. rend. 1900, 130, 376) from α-campholide (V).



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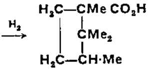
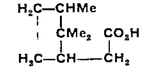


IV.

*iso*Campholic acid has been shown by *von* Braun and Heymons (Ber. 1928, 61, 2276) to be dihydro α campholenic acid (VI).

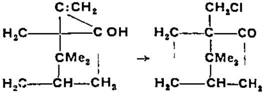


VI.

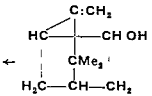
Halogen Derivatives of Camphor.

The direct chlorination of camphor causes substitution on the α-carbon atom, the monosubstitution products existing in two stereoisomeric forms. The two α- and *α′-chlorocamphors*, m.p. 94°, $[\alpha]_D$ +96·2°; m.p. 117°, $[\alpha]_D$ +35°, were first obtained by Lowry and Steele. These compounds show mutarotation in the presence of alkali (J C.S. 1915, 107, 1382). Bromination and nitration of the chloro camphors give stereoisomeric bromo- and nitro-α-chlorocamphors (Lowry, J.C.S. 1898, 73, 569, 584, 987). By the saturation of an alcoholic solution of camphor with chlorine Cazeneuve (Bull. Soc. chim. 1882, [ii], 37, 454) prepared *αα′-dichlorocamphor*, m.p. 96°, $[\alpha]_D$ +57 3°.

β-(or 10-)*Chlorocamphor*, m p. 132 5°, $[\alpha]_D$ +40 7° (III) was prepared by Forster (J.C.S. 1902, 81, 272) by the action of chlorine on hydroxycamphene (I or II).



I. III.



II.

π-Chlorocamphor, m p. 129°–129 5°, $[\alpha]_D$ +99 88°, results when camphor-π sulphonylchloride is heated at 175°–190° (Kipping and Pope, Proc. Chem. Soc. 1895. 11, 213).

aπ-Dichlorocamphor, m.p. 118°–118·5°, is prepared in a similar manner from α-chloro camphor-π- sulphonyl chloride.

α-Bromocamphor, m.p. 76°–77° (*dl*-, m.p. 51 1°), $[\alpha]_D$ +117·1°, is obtained by the addition of bromine to camphor at 100° (Armstrong and Mathews, Chem. News, 1878, 73, 4; Kipping and Pope, J.C S. 1893, 63, 576; Marsh, *ibid.* 1890, 57, 828). The isomeric, *α′ bromocamphor*, m.p. 78°, $[\alpha]_{5461}$ –40°, was first described by Lowry, Steele, and Burgess (J.C.S. 1922, 121, 633). These substances show mutarotation in solution in the presence of alkali (Kipping, Proc. Chem. Soc. 1905, 21, 124).

β-Bromocamphor, m.p. 78°, $[\alpha]_D$ +19 1°, can be prepared from hydroxycamphene (Forster, J.C.S. 1902, 81, 267) or by heating camphor-β-sulphonylbromide (Armstrong and Lowry, J.C S. 1902, 81, 1469) (*see*, however, Lipp and Lausberg, Annalen, 1924, 436, 274).

π-Bromocamphor, two forms, m p. 60°–63° and 93 4° respectively, $[\alpha]_D$ +116 01°, is prepared in a similar manner to its chloro-analogue (Kipping and Pope, J C.S. 1895, 67, 382).

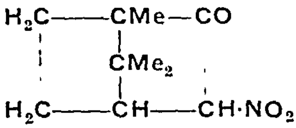
αα′-Dibromocamphor, m.p. 61°, $[\alpha]_D$ +39 2°, can be obtained by brominating α-bromocamphor; *αβ dibromocamphor, m.p. 114°*, $[\alpha]_{5461}$ +127°, from α - bromocamphor - β - sulphonylbromide (Armstrong and Lowry, J.C.S. 1902, 81, 1451).

α′β-Dibromocamphor, m.p. 136°, $[\alpha]_{5461}$ +85° (Burgess and Lowry, J.C.S. 1923, 123, 1873); *aπ dibromocamphor*, m.p. 153°, $[\alpha]_D$ +128 2° are obtained in a similar manner to the chloro derivatives (Kipping and Pope, Proc. Chem. Soc. 1895, 11, 213). Two isomeric tribromocamphors, *αα′β tribromo*, m p. 63°–64°, $[\alpha]_D$ +2°, and *αα′π-tribromo*, m.p. 69°–70°, have been described (Lapworth, J.C.S. 1899, 75, 574).

α-Iodocamphor, m.p. 43°–44°, $[\alpha]_D$ +160 42°, was prepared by Haller (Compt. rend. 1875, 80, 695; 1878, 87, 695, 843, 925) by the action of iodine on sodiocamphor, whilst *αα′-di iodo camphor*, m p. 108°–109°, $[\alpha]_D$ +28°, results from the action of iodine on hydroxymethylene camphor in the presence of alkali (Bruhl, Ber. 1904, 37, 2158).

Nitrocamphor.

α-Nitrocamphor, m.p. 102°, *cannot be prepared* by the direct action of nitric acid on camphor. It is, however, readily obtained when the halogenated nitrocamphors are reduced. It is prepared most conveniently by the reduction of α-bromo-α′-nitrocamphor with an alcoholic solution of sodium ethoxide, the yield being 50% (Lowry and Steele, J.C.S. 1915, **107**, 1038). In solution *α′*-nitrocamphor (I) shows mutarotation (Lowry, J.C.S. 1899, **75**, 211), the initial value in benzene, $[\alpha]_D$ −214°, falling to −104°. This change is due to its conversion into the pseudo-form (II). Pseudonitrocamphor has not been isolated, but its salts are known. When an aqueous solution of *α′*-nitrocamphor is evaporated it yields the *anhydride* of *pseudonitrocamphor*, m.p. 193° (III).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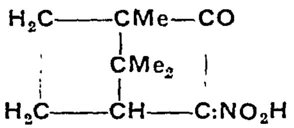
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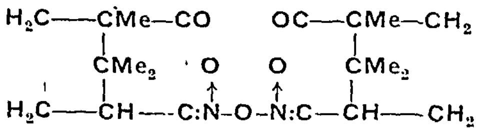
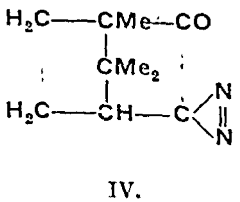

III.

On reduction with sodium amalgam or with zinc dust in acetic acid, *α′*-nitrocamphor gives *α′-aminocamphor*, m.p. 110°–114°, b.p. 246·4° (Schiff, Ber. 1880, **13**, 1404 ; Kachler and Spitzer Monatsh. 1880, **34**, 567) from which by reduction with sodium and alcohol *aminoborneol*, m.p. 187°, is obtained (Duden and McIntyre, Ber. 1898, **31**, 1902, 1900, **33**, 481). The reactions of this base have been studied by Forster and his collaborators (J.C.S. 1905, **87**, 110, 712, 826 ; 1909, **95**, 2057 ; 1914, **105**, 2770). With nitrous acid *α′*-aminocamphor gives *diazocamphor*, m.p. 73° (IV) (Schiff, Ber. 1886, **14**, 1373), which when heated with water passes into *β-peri*cyclo*camphanone* (V), m.p. 168°–170° (Bredt and Holz, J. pr. Chem. 1917, **95**, 133).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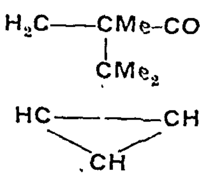

V.

β-Aminocamphor, m.p. 81°, was prepared by Tiemann (Ber. 1895, **28**, 1082 ; 1897, **30**, 321) by the action of hydrogen iodide on camphoroxime and later by Forster and Howard (J.C.S. 1913, **103**, 63) by the action of ammonia on β-bromocamphor. It yields a mixture of two isomeric oximes and two isomeric semicarbazones.

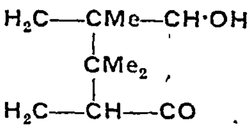
The Camphor Sulphonic Acids.

Camphor β-sulphonic acid (Reychler's acid), m.p. 192°–193°, is readily prepared by the action of sulphuric acid on camphor in acetic anhydride solution (Reychler, Bull. Soc. chim. 1898, [iii], **19**, 120). Its constitution has been determined by Wedekind, Schenk and Stüsser (Ber. 1923, **56**, [B], 640 ; *cf.* Armstrong and Lowry, J.C.S. 1902, **81**, 1444 ; Burgess and Lowry, *ibid.* 1925, **127**, 271 ; Bredt, Rochussen, and Heusch, Ber. 1902, **35**, 1290 (footnote) ; Lipp and Lausberg, Annalen, 1924, **436**, 274). Its salts show mutarotation (Schreiber and Shriner, J. Amer. Chem. Soc. 1935, **57**, 1306, 1445, 1896 ; Sutherland and Shriner, *ibid.* 1936, **58**, 62). The resolution of the *dl*-acid into its optically active enantiomorphs has been studied by Burgess and Gibson (J.S.C.I. 1925, **44**, 296).

dl-*Camphor π-sulphonic acid, acid chloride*, m.p. 105·5°–106·5° ; *amide*, m.p. 133·5°–136·5°, is obtained when camphor is treated with fuming sulphuric acid, the camphor being racemised (Kipping and Pope, J.C.S. 1893, **63**, 549 ; 1895, **67**, 357). It can be separated into the *d*- and *l*-forms by strychnine (Pope and Read, J.C.S. 1910, **97**, 992).

The Hydroxycamphors.

α-(or 3-)*Hydroxycamphor* (II), *d*-, m.p. 197°–198°, $[\alpha]_D$ +17·3°, *semicarbazone*, m.p. 183°–184°; *dl*-, m.p. 200°, *semicarbazone*, m.p. 182°–183°, was prepared by Manasse (Ber. 1897, **30**, 659) by the reduction of camphor-quinone (I) with zinc dust in acetic acid solution, when it is found in admixture with a second hydroxy ketone, *hydroxyepicamphor* (III). Later α-hydroxycamphor was obtained by Lapworth and Chapman (J.C.S. 1901, **79**, 384) by heating hydroxycamphorcarboxylic acid (IV). The *constitution of Manasse's two hydroxycamphors* was subsequently investigated by Karrer and Takashima (Helv. Chim. Acta, 1925, **8**, 2112), Forster and Shukla (J.C.S. 1925, **127**, 1885), and by Bredt and his collaborators (J. pr. Chem. 1926, [ii], **112**, 273 ; 1929, [ii], **121**, 153 ; 1931, [ii], **131**, 49 ; Ber. 1929, **62**, [B], 2314).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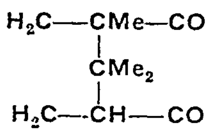
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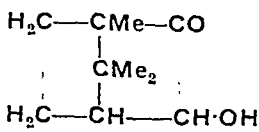
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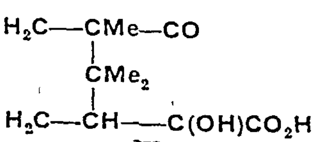
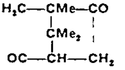

IV.

4-*Hydroxycamphor*, m.p. 250°, *semicarbazone*, m.p. 236°–238°, was prepared by Houben and Pfankuch (Annalen, 1931, 489, 192) from 4 aminocamphor.

5-*Hydroxycamphor*, m.p 216°–217°, $[\alpha]_D$ +38 9°, is excreted in admixture with 3- and π hydroxy-camphors in the urine of dogs fed on a diet containing camphor (Schmiedeberg and Meyer, Z. physiol. Chem. 1879, 3, 422 ; Magnus-Levy, Biochem. Z. 1907, 2, 319 ; Asahina and Ishidate, Ber. 1928, 61, [B], 553 ; 1193, 64, [B], 188 , 1933, 66, [B], 1673 ; 1935, 68, [B], 947 , Reinartz and Zanke, *ibid.* 1935, 68, [B], 548). 5-Hydroxycamphor (I) can be prepared by the hydrogenation of p-*diketocamphane* (II) (Reinartz and Zanke, Ber. 1934, 67, [B], 548) and from β-pericyclo*camphanone* by treatment with trichloroacetic and sulphuric acids at 150°–160° followed by hydrolysis of the 5-tri chloroacetyl derivative with alkali (Takeuchi, Sci. Papers, Inst. Phys. Chem. Res. Tokyo, 1934, 23, 288).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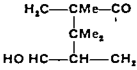
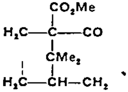

I.

10-*Hydroxycamphor* (I), m.p 220°, $[\alpha]_D$ +48 0°, has been prepared by Asahina and Ishidate (Ber. 1934, 67, [B], 1202) by the reduction of the *semicarbazone* of *methyl ketopinate* (II) with sodium and alcohol. The resulting *semicarbazone*, m p. 200°, giving on hydrolysis the hydroxyketone. On oxidation with chromic acid the *keto aldehyde* (III), m.p. 211°–213°, is obtained.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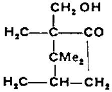
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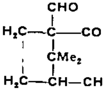
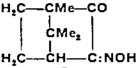

III.

π-*Hydroxycamphors, cis* , m.p. 233°–234°, $[\alpha]_D$ +40 68°, *semicarbazone*, m.p. 216°–217° ; *trans*-, m.p. 233°, $[\alpha]_D$ +62 2°, *semicarbazone*, m p. 224°–225°, have been prepared by Asahina and Ishidate (Ber. 1934, 67, [B], 74) by the reduction with sodium and alcohol of the semicarbazones of *cis*- and *trans*-methyl π-*apo*camphor-7-carboxylate. On oxidation they yield the corresponding *keto-aldehydes*, m.p. 205° and 195°–196° respectively.

The Keto-Camphors.

Camphorquinone (II), m.p. 198°, $[\alpha]_D$ −105 4°, crystallises in golden yellow needles. It was first prepared by the hydrolysis of its monoxime, *isonitrosocamphor* (I), which is formed when sodiocamphor is treated with *iso*amyl nitrite (Claisen and Manasse, Annalen, 1893, 274, 530 ; Rupe and Splittgerber, Ber. 1907, 40, 4313). *iso*Nitrosocamphor is obtained also by the action of nitrous acid on camphorcarboxylic acid (Oddo, Gazzetta, 1893, 23, 187) and by the action of *iso*amyl nitrite on α-bromocamphor (Clarke, Lapworth, and Wechsler, J.C.S. 1908, 93, 40).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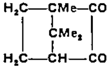
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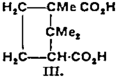
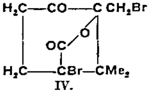

III.

The hydrolysis is most readily carried out by digestion with formaldehyde and hydrochloric acid (Lapworth, J.C.S. 1907, 91, 1134). Camphorquinone is, however, most conveniently prepared by the oxidation of camphor in acetic anhydride solution with selenium dioxide (Evans, Ridgion, and Simonsen, J.C.S. 1934, 137). The constitution of camphorquinone is proved by its oxidation with hydrogen peroxide to camphoric acid (III) (Forster and Holmes, J.C.S. 1908, 93, 252), a ring fission which occurs also by digestion with alcoholic potassium hydroxide solution (Claisen and Manasse, *l.c.*). On reduction with zinc dust and acetic acid or with aluminium amalgam a mixture of hydroxycamphor and hydroxyepicamphor is obtained (*see above*). Reduction of this mixture with sodium and alcohol gives *camphor glycol*, m.p. 230°–231°, $[\alpha]_D$ +12·3°.

On bromination camphorquinone gives a *dibromide*, $C_{10}H_{12}O_2Br_2$, *m.p.* 137°–138°, and a *tribromide*, $C_{10}H_{11}O_2Br_3$, m.p. 197°–198° (Manasse and Samuel, Ber. 1897, 30, 3160). These bromides have been shown by Evans, Simonsen, and Bhagvat (J.C.S. 1934, 444), to have the *lactone* structures represented by (IV) and (V) respectively.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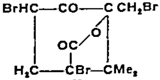
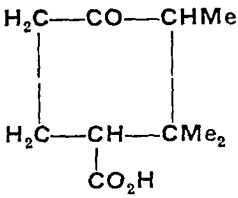

V.

When dissolved in concentrated sulphuric acid camphorquinone gives a *keto-acid*, $C_{10}H_{16}O_3$ (Manasse and Samuel, Ber. 1897, **30**, 3157; 1902, **35**, 3831) which has been shown to be *d*-2:2:3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylic acid* (VI) (Gibson and Simonsen, J.C.S. 1925, **127**, 1295; Bhagvat and Simonsen, *ibid.* 1927, **79**; Bredt-Savelsberg, Zaunbrecher, and Knieke, Ber. 1927, **60**, 1801).



VI.

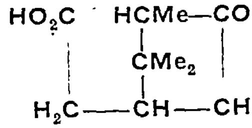
On fusion with alkali camphorquinone yields the *semi-aldehyde* of camphoric acid, m.p. 76°–78°, $[\alpha]_D$ +103·01° (Bredt, J. pr. Chem. 1917, **95**, 63). Camphorquinone can give rise to four monoximes, which are respectively *iso*nitrosocamphors and *iso*nitrosepicamphors. These, together with the related dioximes, have been prepared by Forster and his collaborators (*inter al.*, Forster, J.C.S. 1913, **103**, 662); the configurations assigned to them require modification in the light of more recent investigations (Taylor, J.C.S. 1931, 2021; Meisenheimer and Theilacker, Annalen, 1932, **493**, 33). The melting-points and rotatory powers of these oximes and dioximes are given in the following table:

	M.p.	$[\alpha]_D$
α-*iso*Nitrosocamphor . . .	152°	196·6°
β- " . . .	114°	172·9°
α-*iso*Nitrosoepicamphor . .	170°	−200·1°
β- " . .	137°	−179·4°
α-Dioxime	201°	−63·6°
β- "	248°	−24·1°
γ- "	136°	+22·4°
δ- "	199°	+75·5°

The isomeric semicarbazones, hydrazones, and phenylhydrazones have also been studied by Forster and his collaborators (*inter al.*, J.C.S. 1910, **97**, 2156; 1914, **105**, 1718). The bis-imino-derivatives of camphor have very high rotatory powers, thus *p*-phenylenebisiminocamphor has $[\alpha]_D$ +1509° giving a molecular rotatory power of 6096° (Forster and Thornley, J.C.S. 1909, **95**, 942; Forster and Spinner, *ibid.* 1919, **115**, 891; Singh, *ibid.* 1920, **117**, 1599; 1921, **119**, 1972).

p-*Diketocamphane* (5-*ketocamphor*), m.p. 206·5°–207°, $[\alpha]_D$ +103·42°, *disemicarbazone*, m.p. above 262°, is obtained by the oxidation of 5-hydroxycamphor (Bredt and Goeb, J. pr. Chem. 1921, [ii], **101**, 273) or by the oxidation of camphor by chromic acid in acetic acid solution (Bredt. *ibid.* 1923, [ii], **106**, 336). The reactions of this diketone have been studied by Asahina and Ishidate (Ber. 1934, **67**, [B] 440).

6-*Ketocamphor*, m.p. 194°–195°, *dioxime*, m.p. 241°–242°, *disemicarbazone*, m.p. 228°, was prepared by Miyake and Watanabe (Proc. Imp. Acad. Tokyo, 1935, **11**, 322) by heating the *methyl ester* of (I) at 280°–300°. It can be hydrolysed to the parent acid.



I.

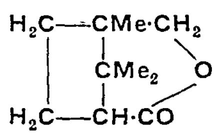
Camphoric Acid.

Camphoric acid has been prepared in four stereoisomeric forms, the melting-points and rotatory powers being given in the table below:

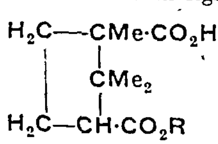
	M.p.	$[\alpha]_D$
d-Camphoric acid . .	187°	+47·8°
l- " "	187°	−47·8°
dl- " "	202°–203°	—
d-*iso*Camphoric acid . .	171°–172°	−47·1°
l- " " . .	171°–172°	+47·1°
dl- " " . .	191°	—

d-Camphoric acid, which has the *cis*-configuration, is obtained by the oxidation of *d*-camphor and is isomerised to *d*-*iso*camphoric acid by heating with water at 200°–220° (Jungfleisch, Ber. 1873, **6**, 680), by heating with hydrochloric acid at 150°–160° (Wreden, Annalen, 1872, **163**, 328) and by fusion with potassium hydroxide (Mahla and Tiemann, Ber. 1895, **28**, 215). The two acids are readily separated by treatment with acetyl chloride when *d*-camphoric acid yields the *anhydride*, m.p. 220°–221° (Aschan, Ber. 1874, **27**, 2001; Annalen, 1901, **316**, 209). The synthesis and the proof of the structure of camphoric acid has been given above.

Reduction of camphoric anhydride with sodium amalgam (Haller, Bull. Soc. chim. 1896, [iii], **7**, 984) or catalytically (Rupe and Jäggi, Helv. Chim. Acta, 1920 **3**, 654) gives *α-campholide*, whilst reduction of β-methyl hydrogen camphorate gives *β-campholide*, m.p. 218°–220°:



Being unsymmetrical camphoric acid gives two hydrogen esters, the α-(or *ortho*-) *esters* (I) (*α-methyl hydrogen camphorate*, m.p. 77°) and the β- (or *allo*-) *esters* (II) (*β-methyl hydrogen camphorate*, m.p. 86°–87°). The structures of these esters have been rigidly proved (Walker, J.C.S. 1892, **61**, 1093; 1893, **63**, 415; Walker and Henderson, *ibid.* 1895, **67**, 337; Blanc, Bull. Soc. chim. 1899, [iii], **21**, 716; Brühl and Braunschweig, Ber. 1892, **25**, 1086).



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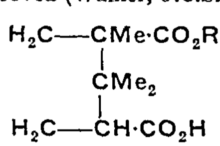
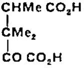


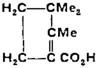
II.

Two *monoamides* have been prepared, α-, m p. 176°–177°, by the action of ammonia on the anhydride and β, m.p. 182°–183°, by treating *camphorimide*, m.p. 243°–244°, with dilute sodium hydroxide. Camphorimide is readily obtained by heating the α amide or by passing ammonia into the molten anhydride.

Camphoric acid is extremely stable to oxidising agents On prolonged heating with nitric acid it gives camphoronic acid, whilst with potassium permanganate in alkaline solution Balbiano's acid is obtained, which has been shown by Bardhan (J.C S. 1928, 2604) to be represented by (III).



III.



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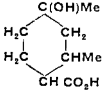
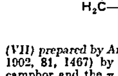


V.

With aluminium chloride camphoric acid gives *iso*lauronolic acid (IV) and four isomeric 1 *hydroxy* - 1 3 *dimethyl*cyclohexan - 4 *carboxylic acids* (V) (Lees and Perkin, J C S 1901, 79, 332 ; Perkin and Yates, *ibid.* 1373) On treatment with chlorine or bromine camphoric acid gives the corresponding monosubstituted anhydrides, *α chlorocamphoric anhydride*, m p 233°–235°, and *α bromocamphoric anhydride*. Both these anhydrides give on digestion with water or with alkali the lactonic acid, *camphanic acid* (VI). Two other monobromo acids are known, *β bromocamphoric acid*, m p 209°–210°,



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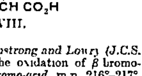

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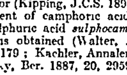
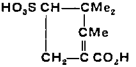


VIII.

(VII) *prepared by Armstrong and Lowry* (J.C.S. 1902, 81, 1467) by the oxidation of β bromocamphor and the *π bromo-acid*, m.p. 216°–217°, (VIII), obtained by the oxidation of *απ*-di bromocamphor (Kipping, J.C.S. 1896, 69, 913).

By treatment of camphoric acid with concentrated sulphuric acid *sulphocamphylic acid*, $C_9H_{14}O_5S$, is obtained (Walter, Ann. Chim. 1843, [iii], 9, 179 ; Kachler, Annalen, 1873, 169, 179 ; Damsky, Ber. 1887, 20, 2959 ; Koenigs and Hoerlin, *ibid.* 1893, 26, 812 ; 1894, 27, 3466 ; Perkin, J C.S. 1898, 73, 798 ; 1903, 83, 835). This acid has been shown by Lewis and Simonsen (J C.S. 1937, 457) to have the structure (IX). On fusion with potassium hydroxide it gives *α camphylic acid* (X), m p. 148°, and *β-camphylic acid* (XI), m p. 105°–106° (Lewis and Simonsen, J.C S. 1936, 734).



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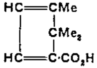
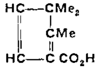


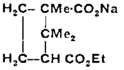
X.



XI.

The following acids have been prepared from camphoric acid by elimination of one of the carboxyl groups

α Campholytic acid (XII), b p 240°–243°, *amide*, m p. 103°, was prepared by Walker (J C S 1893, 63, 493) by the electrolysis of the sodium salt of α-ethyl hydrogen camphorate (XIII) It has been prepared also by Noyes



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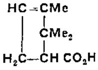
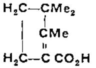


XII.



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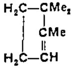
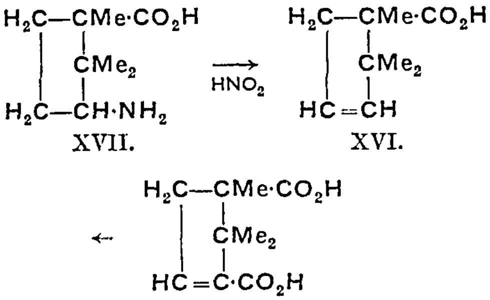


XV.

(Amer. Chem. J. 1894, 16, 500 ; 1895, 17, 424 ; 1902, 24, 290 ; Noyes and Potter, J. Amer. Chem. Soc. 1902, 34, 1067). It was synthesised by Perkin and Thorpe (J.C S. 1904, 85, 147) from *α* campholactone. Its most characteristic reaction is its isomerisation to *iso*lauronolic acid (XIV), m p 135 , by the action of cold concentrated sulphuric acid or by warming with the dilute acid This acid, known also as β-campholytic acid and *iso*campholytic acid, was first obtained by Walker (J.C.S. 1893, 63, 504) as a by product in the electrolysis of the sodium salt of α-ethyl hydrogen camphorate (XIII). Reference has been made above to its formation by the action of aluminium chloride on camphoric acid. When treated with hydrobromic acid it gives the hydrobromide of α campholytic acid. When *iso*lauronolic acid is heated at 300° it gives the hydrocarbon *iso*laurolene (XV), b p. 108 5°/758 mm., d_{15}^{15} 0 7867, n_D^{20} 1·4333 (Blanc, Bull. Soc. chim 1898, [iii], 19, 200 ;

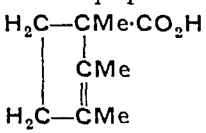
Ann. Chim. 1899, [vii], 18. 215 ; Compt. rend. 1906, 142, 1085).

Camphonenic acid (γ-*lauronolic acid*), m.p. 155°–156° (XVI), was first prepared by the action of nitrous acid on *aminocamphonanic acid* (XVII) (Noyes, Ber. 1895, 28, 583 ; Amer. Chem. J. 1894, 16, 508 ; 1895, 17, 433), but it is obtained most readily by heating dehydrocamphoric acid (XVIII).



XVII. XVI. XVIII.

Laurolenic acid (originally called *lauronolic acid*, Fittig and Woringer, Annalen, 1885, 227, 1), m.p. 13°, b.p. 135°–135·5°/14·5 mm. (XIX), is most readily prepared by heating α-chlorocamphoric anhydride with water or with sodium carbonate solution (Bredt and Amann, J. pr. Chem. 1913, [ii], 87, 12 ; Aschan, Ber. 1894, 27, 3540). It has been prepared also by other



XIX.

reactions and the structure now assigned to it was suggested by Lapworth (Brit. Assoc. Reports, 1900, 327 ; Lapworth and Linton, J.C.S. 1901, 79, 1284). J. L. S.

CAMPHOR, ESSENTIAL OIL OF. Camphor oil is distilled from all parts of the camphor tree, *Cinnamomum camphora* Nees and Eberm. (Fam. Lauraceæ), which is indigenous to China and Japan. It has been cultivated in India, Ceylon, Java, the Malay Archipelago, Australia, east and south Italy, Algiers, California, Florida, the West Indies and Mauritius. The tree grows to a height of 60–100 ft. In Japan and Formosa it is chiefly distilled for the production of camphor, and 70% of the world's supply is obtained from this source. Camphor oil is a by-product after the extraction of camphor and safrole, which are separated by fractional distillation and freezing. Oil from the leaves is rich in camphor, and a continuous supply is available. Oil from the wood and root contains more safrol. The crude camphor oil has sp.gr. 0·950–0·990, and yields two products on fractional distillation—white camphor oil (sp.gr. 0·875–0·900) consisting of the lower boiling fractions, and brown camphor oil (sp.gr. 1·018–1·026) containing 25–35% of safrole.

Constituents.—In addition to camphor and safrole, *d*-α-pinene, β-pinene, *d*-limonene, *d*-fenchene, phellandrene, cineole, borneol, terpineol, citronellol, cuminol and small quantities of geraniol and linalol have been isolated. Piperitone, carvacrol, eugenol, ethylguaiacol, limene, cadinene, α-camphorene, and traces of esters have also been found.

Characters.—Camphor oil has sp.gr. 0·875–0·900 at 15·5°, α_D^{20} +9° to +24°, n_D^{20} 1·465–1·470. Contains about 35% of cineole. This oil is used in medicine as a mild counter-irritant for rheumatism. Brown camphor oil is chiefly used as a source of safrole. C. T. B.

CAMPHOR, SYNTHETIC. Synthetic camphor, as it is usually known, cannot be regarded as suitably named; since the commercial product is derived from a naturally occurring substance, pinene, which possesses the same number of carbon atoms in the molecule and has never been completely synthesised. True synthetic camphor is known but only as a laboratory preparation. In conjunction with the growth of the celluloid industry, in which camphor is chiefly used, camphor manufacture has developed on an increasing scale, for although in the early days of the celluloid industry sufficient natural camphor was available, the use of synthetic camphor predominates at the present day. Synthetic camphor has been made on an industrial scale since the beginning of this century, but its importance was first realised at the time of the Russo-Japanese War of 1904–1906, when natural camphor became scarce and prices rose to very high levels. Commercial synthetic camphor, originally made in Germany, has since been made also in England, the U.S.A., France, Italy, Switzerland, Spain, and the U.S.S.R.

Raw Materials.

The chief raw material is pinene, which is obtained from the oleo-resin of pine trees, oil of turpentine consisting principally of α- and β-pinene. For the purposes of camphor manufacture a raw material containing a high proportion of pinene is essential, and although most of the types of pines commercially exploited for turpentine yield a suitable essence, certain varieties do not; Indian turpentine, for instance, from *Pinus longifolia*, contains only 35% of pinene. Greek, Spanish, and Portuguese turpentines give an oil containing about 90% of α-pinene, with very little β-pinene. French and American turpentine, on the other hand, contain 90% of pinene, of which 30% is β-pinene and the remainder α-pinene. α- and β-Pinene are both suitable as sources of camphor, although in some processes β-pinene is more reactive and gives higher yields of camphor than α-pinene.

Another source of pinene is from steam-distilled wood turpentine, an industry developed in the U.S.A. in recent years. Pine stumps from cut-over lands are shredded and steam-treated, liberating rosin, pine oil, and steam-distilled wood turpentine, the latter containing about 70% α-pinene, together with dipentene, terpinene, etc. By fractional distillation a grade of α-pinene is obtained which is claimed to be 98% pinene. Previously wood turpentine, prepared by destructive distillation, was very low in pinene content, and contained in addition objectionable by-products from the pyrolysis of the wood and rosin.

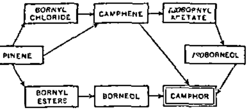
Substitutes are available for turpentine in many of its uses, but it is irreplaceable as a raw material for camphor manufacture. It is, therefore, important to note that there is no source of turpentine in this country. The Scotch fir yields an oil containing pinene, but the climate is unfavourable for rapid tree growth and easy flow of gum essential for successful turpentine operations. Within the British Empire, West Australia is regarded as possessing a suitable climate, but the establishment of pine forests would require many years. India contains, in addition to *Pinus longifolia* already referred to, large tracts of Himalayan Blue Pine (*Pinus excelsa*) capable of yielding a high grade of α-pinene, but as yet almost unexploited owing to the inaccessibility of the forests. In Great Britain, pinene, or oil of turpentine, as a light hydrocarbon oil, is subject at the present time (1937) to an import duty of 8*d.* per gallon, the tax representing about 25% of the total cost

As pinene is liable to oxidation if exposed to air, storage of turpentine has always been a serious problem. It is the normal practice to transport it in wooden barrels lined with glue, and turpentine so transported can be relied on to arrive in good condition, without excessive leakage. When consigned to merchants, the turpentine is tanked at the docks, as the barrels cannot be stored for any length of time without developing leaks. When sold, the turpentine is run out into the original barrels, but in the meantime has undergone some oxidation with a corresponding diminution in pinene content. In order to reduce the tendency to discolour, the tanks are often lined with shellac, discoloration being due to attack on the iron by the small quantities of acids produced during atmospheric oxidation of the pinene; but even so deterioration is unavoidable and turpentine which has been tanked is generally regarded as unsuitable for camphor manufacture.

Gum turpentine may be supplied in galvanised drums, but does not arrive in such good condition as when packed in wooden barrels, the zinc coating being slowly attacked. Pinene from steam-distilled wood turpentine, on the other hand, does not attack galvanised drums appreciably and may be stored for periods up to 6 months without apparent deterioration if air is excluded.

The empirical formulæ of camphor ($C_{10}H_{16}O$) and pinene ($C_{10}H_{16}$) differ by one oxygen atom, but oxidation of pinene to camphor, although claimed in numerous patents, is not practicable, and the conversion has to be carried out by indirect methods. The chief difficulties in the conversion of pinene to camphor are due to the high reactivity of pinene, and the fact that none of its additive reactions proceeds without the simultaneous occurrence of side reactions. For this reason, and also on account of the volatility of the terpenes, the yield of camphor is not quantitative, and in comparing various processes from an economic standpoint this is a very important factor, pinene being by far the largest single item in the total cost.

In the majority of processes pinene is treated with an acid, yielding an ester of borneol. This is converted into either borneol or camphene, which is then oxidised to camphor. The processes which have been developed are represented in the following scheme:

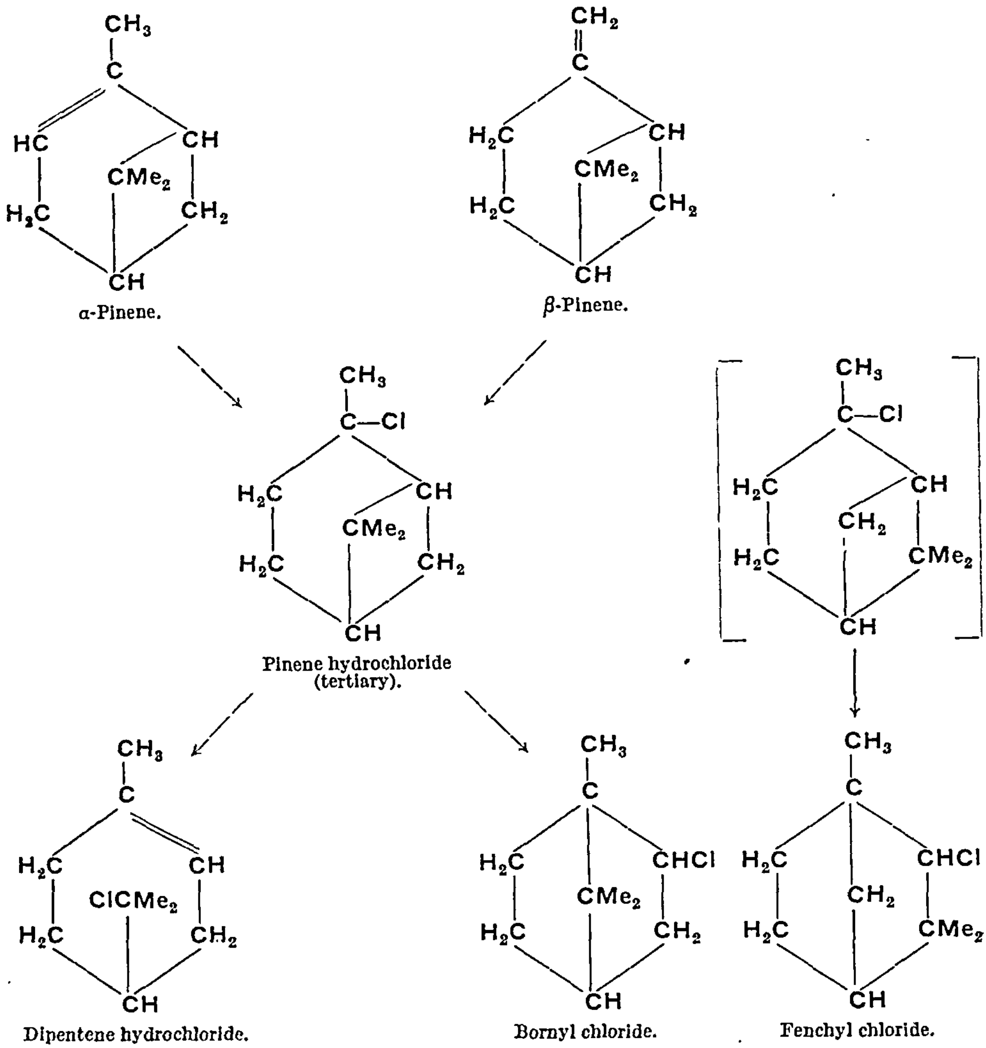


Those methods depending on the formation of bornyl chloride and camphene, followed by oxidation to camphor, either directly or after conversion of camphene to *iso*borneol, constitute what may be described as the classical process, which the firm of Schering, pioneers in large-scale camphor manufacture, have developed in Germany This process, with variants, is now described in some detail, after which the alternative processes are reviewed.

Pinene—Bornyl Chloride.—The action of hydrogen chloride on pinene yields a crude product containing principally bornyl chloride, together with by products such as dipentene hydrochloride and fenchyl chloride. This reaction depends on the addition of the elements of hydrogen chloride to form a tertiary hydrochloride, followed by rearrangement of the molecule. As will be seen from the equations, the rearrangement may take place either to dipentene hydrochloride, bornyl chloride, or fenchene hydrochloride, the last being more easily visualised when the formula for pinene is written with the *cyclo*butane ring reversed. Fortunately for camphor manufacturers bornyl chloride predominates, as much as 70% of the pinene being recovered in this form. Fenchene hydrochloride normally occurs to the extent of about 3% but may be higher. If oil of turpentine is employed it is usually redistilled, preferably under vacuum, and the pinene dried over calcium chloride or quicklime. This distillation removes most of the sesquiterpenes and other high-boiling impurities.

The distilled pinene in batches of not more than 1 ton is saturated with dry hydrogen chloride in lead-lined or enamelled vessels fitted with powerful stirrers and brine jackets. Refrigeration is essential to prevent the considerable heat of reaction, causing undue rise in temperature. In the first stages of the reaction the temperature is kept at 0°–10°, but later rises to 35°, when the bornyl chloride begins to crystallise By this time the pinene has absorbed about 22% of its weight of hydrogen chloride but subsequently continues to absorb the gas more slowly. When all the pinene has disappeared the gas absorption is still less than one equivalent owing to the fact that the relatively unstable dipentene hydrochloride formed in the early stages reacts to some extent with fresh pinene, and thus the finished product may contain free dipentene. It is possible to continue the saturation beyond this point, but there is no advantage to be gained, as the bornyl chloride content cannot be increased.

As already mentioned, temperature control is



very important, and the temperature should not in any case exceed 50°. Very low temperatures, on the other hand, are not necessary, and there is evidence that such conditions lead to a lowering of yield. There does not appear to be any catalyst which increases the yield of bornyl chloride, but many substances have an adverse effect. Metals, especially iron, have a pronounced effect, especially if water is also present. In contact with metallic iron, or if ferric chloride is added to the pinene, the yield of bornyl chloride is so much reduced that the product, normally a pale straw colour and semi-solid, is a dark reddish liquid with an excessively high content of hydrogen chloride, the catalyst favouring the continued reaction of dipentene to the dihydrochloride stage. The use of lead for the reaction vessels is permissible owing to the formation of an adherent coating of lead chloride over the surfaces exposed to the gas, but a reduced yield may be expected in the first few batches from a new lead-lined pot.

Water is also found to have a deleterious action, but this is not pronounced in the absence of other catalysts. The formation of fenchyl chloride is said to be more noticeable in the presence of water. Precautions are therefore taken to dry the pinene and the gas used for saturation. It is also necessary to eliminate from the pinene those substances which may liberate water during the course of the reaction. Pinene readily oxidises in the presence of air, yielding pinene peroxide, verbenone, etc., all of which are capable of liberating water by decomposition. Other oxidation products of pinene such as acetic and formic acids are also harmful.

An important part of this process is the preparation of the hydrogen chloride. Synthetic hydrogen chloride made by burning chlorine in hydrogen is not suitable as it is accompanied by a considerable amount of water. In small quantities the gas may be prepared by heating commercial muriatic acid with concentrated sulphuric acid, but this is somewhat wasteful. For generating a continuous supply of dry gas the Zahn process is convenient, in which dry granular rock salt and sulphuric acid are fed in the correct

proportions to a cast-iron vessel containing liquid sodium bisulphate maintained at a temperature of 320°C. The gas is liberated almost instantaneously, leaving sodium bisulphate, which, as it accumulates, overflows through a dip pipe reaching to the bottom of the vessel. The gas, which is led off under a slight suction of $\frac{1}{10}$ in. water, is of very high quality (90% or over), and after drying by passing up a sulphuric acid tower may be pumped directly to the saturators. In order to economise in gas these are connected in series, the fresh batch receiving the residual gas. A small quantity of gas is unabsorbed *and is condensed in a water-absorption tower.*

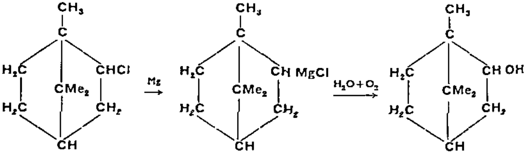
Unless there is an outlet for the sodium bisulphate produced as a by product the Zahn process is rather expensive, and in larger installations a mechanical salt cake furnace (Ind. Chem. 1931, 7, 461) is used as a source of hydrogen chloride, the by-product being readily saleable, and a cheaper grade of salt may be used as a raw material. On the other hand, the salt cake furnace gives a gas containing only 50–60% HCl, the balance being air, and the mixture is more difficult to dry. In presence of air only about half of the gas is taken up by the pinene, and the rest has to be absorbed in water and disposed of.

Several methods are available for treating the product of the reaction between pinene and HCl. As the bornyl chloride crystallises well the product may be filtered and more than half of the bornyl chloride recovered in a solid form; the mother liquor containing about 60% of bornyl chloride may be treated by any of the following methods either singly or in combination

(1) Refrigeration followed by a second filtration.
(2) Resaturation with HCl to reduce the solubility of bornyl chloride in the mother liquor; followed by filtration.
(3) Heating to decompose the less stable dipentene hydrochloride, followed by distillation of the dipentene thus formed.
(4) Oxidation with nitric acid.
(5) Treatment with sulphuric acid to polymerise the dipentene, followed by steam distillation of the bornyl chloride.

None of these methods gives the highest possible yield and some manufacturers defer the separation of the by products, either by passing the whole reaction product forward to the next stage of the process, or by a simple filtration followed by separate treatment of the solid and liquid hydrochlorides in the next process. The "solid pinene hydrochloride" prepared in this way contains about 90% bornyl chloride, and the pure substance can be obtained by *recrystallisation. It is a white crystalline* solid with distinctive odour, m.p. 132°, b p. 207°. When pure it is stable at the boiling point. At one time bornyl chloride was put forward as a camphor substitute under the name "Artificial Camphor," but although it has some gelatinising action on nitrocellulose it has never been used successfully in celluloid manufacture

Bornyl Chloride — Camphene. — Bornyl chloride has the same ring structure as borneol and camphor, but no commercial process has yet been developed for the direct conversion, although several patents are in existence. By treating bornyl chloride with magnesium a Grignard type of compound is obtained which oxidises in presence of oxygen and water to give borneol

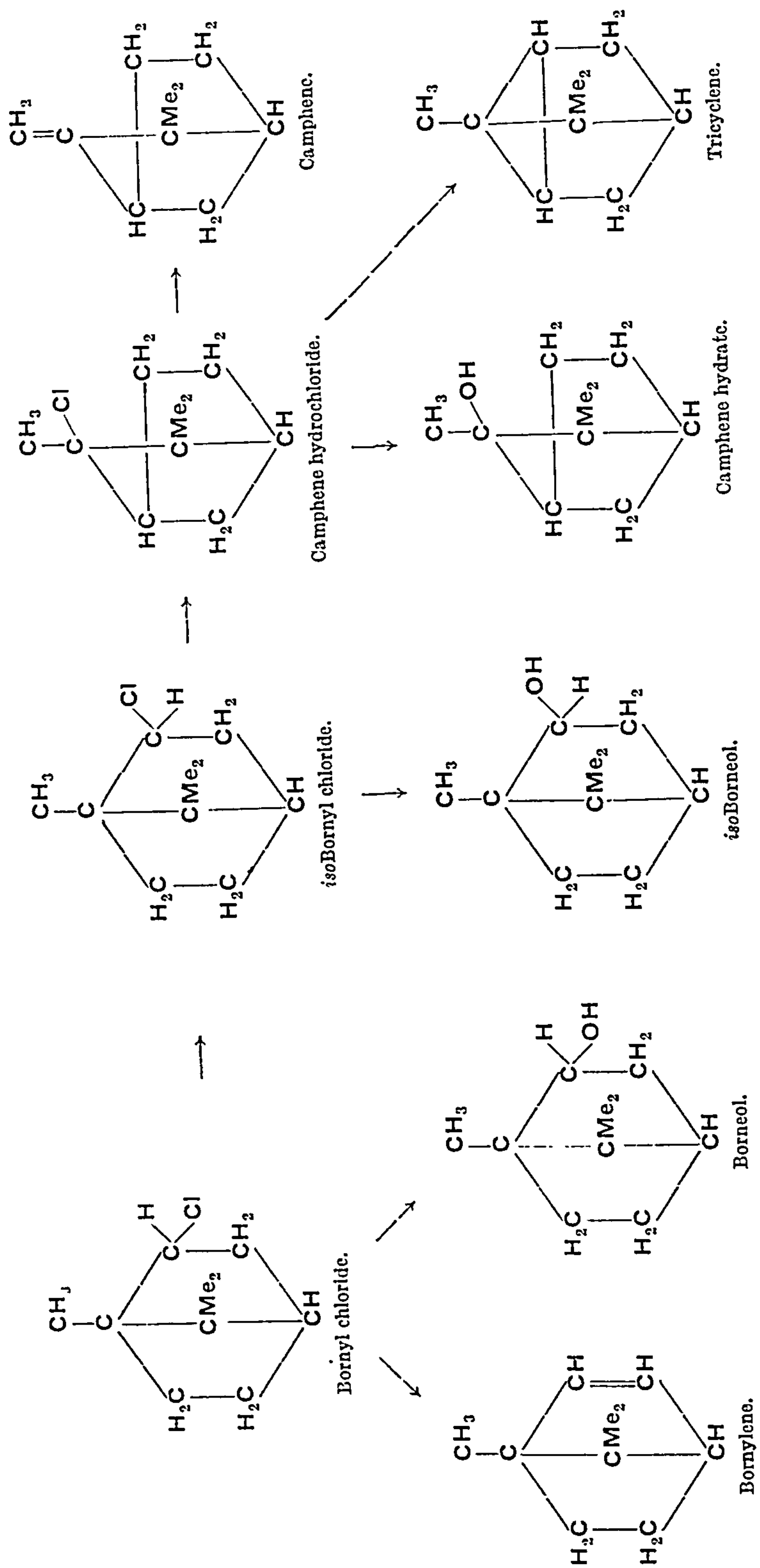


Direct oxidation of bornyl chloride, although claimed to give camphor, fails to remove the chlorine atom and produces *p*-ketobornyl chloride (Bredt and Pinten, J. pr. Chem. 1927, [ii], 115, 45).

Elimination of HCl by direct action of steam in presence of catalysts has been proposed, but in practice bornyl chloride is treated with an alkaline reagent which produces mainly camphene, although smaller quantities of camphene hydrate and borneol are produced. Sodium hydroxide itself is too active a reagent, and at the temperature necessary for the elimination of the chlorine it reacts further with the products causing a diminution of camphene yield. A suspension in water of calcium or magnesium hydroxide may be used, but usually the sodium salt of a weak acid is chosen. Among the reagents proposed in the numerous patents on this subject are sodium stearate, phenate, benzene sulphonate, etc, also ammonia, aliphatic amines, and aniline. These processes are carried out in aqueous solutions and owing to the high temperature necessary (180°–200°) have to be conducted under pressure in autoclaves.

In a typical process pinene hydrochloride is heated with sodium stearate in an autoclave at 180°–200° stirred mechanically. The camphene is then steam distilled leaving stearic acid and a solution of sodium chloride. The latter is run off and a fresh charge of sodium hydroxide solution is added to the stearic acid for the next batch.

The course of the reaction may be expressed in the following scheme :


Camphene.
Tricyclene.
Camphene hydrochloride.
Camphene hydrate.
isoBornyl chloride.
isoBorneol.
Bornyl chloride.
Borneol.
Bornylene.

On the basis of Meerwein's theory the first reaction is the isomerisation of bornyl chloride to *iso*bornyl chloride and camphene hydrochloride. The function of the alkaline reagent is to combine with the hydrogen chloride resulting from the decomposition of the camphene hydrochloride, yielding camphene as the main product. Smaller quantities of borneol, *iso*borneol, and camphene hydrate are obtained by direct action on the corresponding chlorides. As would be expected, the use of aqueous calcium hydroxide gives higher proportions of the hydroxylated compounds. Support for this theory of the dehydrochlorination of bornyl chloride is given by experiments which show that the reaction velocity follows the unimolecular law, and is independent of the concentration of alkali, the slow isomerisation of bornyl chloride being the controlling factor.

In another group of processes the reaction is *carried out in acetic or formic acid solutions.* Among the reagents proposed are sodium, lead, and zinc acetates or zinc formate. *In the acid* solvent the reaction proceeds more rapidly and may be conducted at a lower temperature. A proportion of the camphene is converted during the process into *iso*bornyl acetate or formate, and in consequence of this it is often claimed that there is a direct reaction between the bornyl chloride and, for example, sodium acetate.

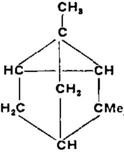
This suggestion can be disproved for the following reasons :

(1) The greater proportion of the bornyl chloride is converted to camphene.
(2) The ester formed is optically inactive.
(3) The ester yields, on hydrolysis, *iso*borneol, and not borneol.
(4) The reaction velocity is unimolecular and independent of the concentration of sodium acetate or similar reagent.

In the conversion of pinene to bornyl chloride and camphene optical activity is retained, *d*-pinene yielding *d*-bornyl chloride and *d*-camphene. When the camphene is converted to esters of *iso*borneol, optical activity disappears except under very special conditions.

At first sight dehydrochlorination in acid solution in presence of sodium acetate is to be preferred, since there is a simultaneous formation of 1 molecule of acetic acid for each molecule of camphene, thus providing sufficient acetic acid for the conversion of the camphene into *iso*bornyl acetate as will be described later. As the acetic acid is afterwards recovered as sodium acetate, which can be used either directly or indirectly in the dehydrochlorination process, the whole process is self contained and does not need a separate acetic acid recovery section which is required when camphene prepared by an alkaline process is esterified to *iso*bornyl acetate. A typical acid process is described in G.P. 268308 ; zinc acetate in acetic acid being the reagent chosen. After dehydrochlorination, the acid layer contains the equivalent amount of zinc chloride, from which zinc acetate is regenerated by addition of sodium acetate, sodium chloride being precipitated and filtered off, while the terpenes are at the same time salted out from the acid layer and may be decanted. In spite of these advantages, however, the acid processes are not used to any extent, the chief obstacle being the difficulty of constructing autoclaves to withstand the severe corrosion.

Camphene, the main product of the dehydrochlorination of bornyl chloride, is associated with small quantities of tricyclene and bornylene, the derivation of these compounds being shown above. In subsequent reactions they behave much the same as camphene. The by products present in the liquid pinene hydrochloride are also dehydrochlorinated during the same process. Dipentene hydrochloride reverts to dipentene, which is further isomerised to terpinene and terpinolene. Fenchyl chloride reacts in a similar series of reactions and may yield any of the five known fenchenes, *cyclo*fenchene being the product most readily isolated from the mixture.



*cyclo*Fenchene

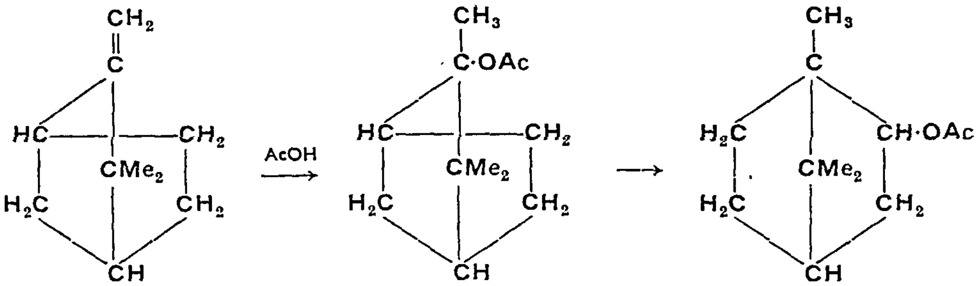
The product from the decomposition of crude pinene hydrochloride has been recently examined in detail by Brus and Vébra (Bull. Inst. Pin, 1936, 73–77, 107–113), who report the presence of many of the above mentioned compounds, and confirm similar work carried out by O. Aschan ("Naphtenverbindungen, Terpene und Campherarten," W. de Gruyter and Co. 1929, p. 235). It is very important to ensure the highest possible degree of elimination of chlorine, and owing to the stability of bornyl chloride, unusual in a non aromatic derivative, this necessitates severe reaction conditions. Pure bornyl chloride is dechlorinated more readily than the crude mixture, and it is possible that the last traces of chlorine which are difficult to remove are combined in one of the by-products

If the dehydrochlorination process has been carried out under optimum conditions, the yield of camphene should be quantitative ; but unless the bornyl chloride has been separated and purified before dehydrochlorination, the product is an oil containing, in addition to camphene, dipentene, terpinene, terpinolene, and some polymers (diterpenes, etc.), also small quantities of fenchene, tricyclene, and bornylene. Camphene may be separated at this stage in a comparatively pure form by fractional distillation, but the separation is difficult on a large scale owing to the closeness of the boiling-points of camphene and the by-products with which it is associated. It is not essential to separate camphene at this stage since the crude product may be treated as such in the next process.

Esterification of Camphene.—The discovery that camphene is converted to *iso*bornyl

acetate by treatment with acetic acid in the presence of a catalyst was made by Bertram and Walbaum (J. pr. Chem. 1894, [ii], 49, 1). This reaction takes place readily at temperatures between 30° and 50°, and gives an excellent yield, although, owing to the fact that the reaction is reversible, some camphene is unchanged unless a large excess of acetic acid is used. A detailed investigation of this reaction has been carried out by Brus and Vébra (Bull. Inst. Pin, 1936, 8, 57, 73). If the dehydrochlorination process has been conducted in acetic acid solution, the camphene is already partly esterified and contains, in addition, some free acetic acid. Various modifications of the Bertram and Walbaum method have been proposed. Catalysts such as phosphoric acid and zinc chloride have been suggested as alternatives to sulphuric acid. The formic acid ester of *iso*borneol is made in a similar way although the use of a catalyst is not essential in this case. Other organic acids such as oxalic have also been proposed for esterifying camphene.

The term esterification is not strictly applicable to this reaction, which comprises empirically the addition of the elements of acetic acid to camphene. Actually a series of reactions is involved ; first of all camphene combines with acetic acid giving the acetic acid ester of camphene hydrate, which isomerises to the *iso*bornyl acetate.



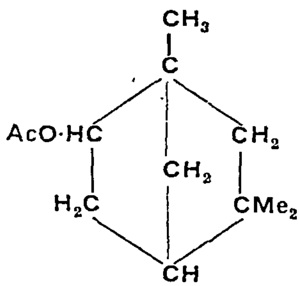
Camphene. Intermediate compound. *iso*Bornyl acetate.

This explanation of the interconversion of camphene and borneol derivatives is due to Meerwein, but the intermediate camphene hydrate ester has never been isolated, and the series of reactions is probably still more complex in the presence of sulphuric acid as a catalyst. Tricylene behaves similarly to camphene giving esters of *iso*borneol, but bornylene gives esters of borneol.

In order to complete the reaction a considerable excess of acid is necessary as the reaction is to some extent reversible. This acid may be removed by washing with water or by distillation under vacuum. The latter method is open to the objection that the bornyl esters, particularly the formate, are liable to decompose on heating, especially in presence of a catalyst. Alternatively the acid may be neutralised with sodium carbonate solution and separated by decantation.

At this stage the ester may be isolated in a pure state by fractional distillation under high vacuum, a process which has been described by Tomeo (Anal. Fís. Quím. Tecn. 1928, 26, 30). Camphene distils first, followed by dipentene, terpinene, etc. Diterpenes remain behind after the ester is removed. Owing to the closeness in boiling points, it is difficult to obtain sharp cuts between the various constituents. *iso*Fenchyl esters, if present, tend to accumulate in the first runnings of the ester fraction and may be partially separated. Pure *iso*bornyl acetate is a colourless liquid with a characteristic pine odour, and is used to some extent in perfumery. It boils at 225° with slight decomposition at atmospheric pressure.

If pure camphene has been used the resultant ester may be 90% pure or over, but if no separation of by-products has been attempted in the earlier stages the ester content is only 70–75%, the balance being unesterified camphene, dipentene, terpinene, terpinolene, and diterpenes, the latter derived from dipentene which tends, in the presence of acid, to undergo isomeric changes leading finally to polyterpenes of unknown composition. Hydrocarbons of the fenchene series, if present, are converted in an analogous way into *iso*fenchyl esters.



*iso*Fenchyl acetate

It is desirable to emphasize at this stage the remarkable change which ring structure undergoes in order to produce the third type of hydrocarbon of the formula $C_{10}H_{16}$. The formula C_nH_{2n-4} requires either 3 double bonds, 1 ring and 2 double bonds, 2 rings and 1 double bond or three rings. The terpenes belong only to the second and third series whilst members of the tricyclic group only occur as intermediate products. Nevertheless, the elimination of the acetyl group may occur in several ways, in accordance with the structure of the hydrocarbon and it is this which makes research in this field so difficult.

The yield of *iso*bornyl ester from camphene depends solely on the amount of camphene left unesterified, unless the concentration of acid catalysts is excessively high, when it is possible to polymerise the camphene to some extent. *iso*Bornyl esters prepared by this method are normally inactive, but Meerwein and Gerard (Annalen, 1924, 435, 189) have succeeded in obtaining active *iso*bornyl esters by working at low temperatures

*iso*Borneol.—The esters of *iso*borneol are hydrolysed quantitatively by alkaline hydroxides. The reaction takes place very readily in alcoholic solution, although *iso*bornyl formate is rapidly hydrolysed on refluxing with aqueous sodium hydroxide. The acetate is more stable and hydrolysis in aqueous solution is usually carried out under pressure at about 180° to complete the reaction Pure *iso*bornyl acetate gives a solid product after running off the aqueous layer, but if the crude ester is hydrolysed direct the product is a liquid, from which *iso*borneol crystallises on cooling, and is filtered off The mother liquor, or " Borneol Oil " as it is usually known, contains up to 60% *iso*borneol, which it is desirable to recover. This is accomplished by distilling off the lighter constituents, after which a further quantity of *iso*borneol may be crystallised.

Owing to the tendency of terpenes to form mixed crystals, *iso*borneol does not crystallise in a pure state from the "Borneol Oil," and may contain about 10% of impurities. *iso*Fenchyl alcohol concentrates in the mother liquors, and after repeated working up for *iso*borneol there *is finally left an inseparable mixture of isoborneol* and *iso*fenchyl alcohol. *iso*Borneol is readily recrystallised from light petroleum and may be obtained ultimately in a pure state. It is, however, difficult to remove completely traces of bornyl chloride usually present in *iso*borneol.

It is possible to obtain *iso*borneol direct from camphene by hydration with aqueous sulphuric acid (F.P. 385341). This process has been examined by Aschan (Finska Kem. Medd. 1929, 38, Årg. Nos. 3 and 4, 94), but the yields appear to be too low for commercial development.

Recovery of Acetic Acid or Formic Acid.—To ensure commercial success it is necessary to recover the highest possible proportion of the acid used in esterification. In a small scale process the production of sodium acetate as a by-product is not embarrassing as it may be readily crystallised and sold. The market, however, is very limited, and on a large scale it is more profitable to utilise the salt as a source of acetic acid for the esterification process. As already shown, this sodium acetate finds an outlet in the acid dehydrochlorination process, but otherwise it is converted to acetic acid in a separate part of the plant. The dried salt being decomposed by sulphuric acid in cast iron vessels fitted with powerful stirrers and the acetic acid then distilled off under vacuum from the residual sodium sulphate. Formic acid may be regenerated in a similar way, taking precautions to avoid decomposition of formic acid to carbon monoxide.

Oxidation of *iso*Borneol and Borneol.—This is an oxidation of a secondary alcohol to a ketone but is complicated by the instability of *iso*borneol, acids readily converting it into camphene and water. Almost every known oxidising agent has been proposed for this reaction, but the only substances suitable for large scale use are nitric acid or chromic acid Mild oxidising agents have no action on *iso*borneol, but on the other hand it is possible to carry the oxidation beyond the ketone stage if the reagent used has a very high oxidation reduction potential or if the conditions are not rigidly controlled. Concentrated nitric acid reacts violently with splitting of the molecule. Dilute nitric acid has been employed, but the product is never completely satisfactory as it contains small quantities of substances which reduce its stability to light and heat. The yield, using nitric acid, is also substantially lower than the theoretical figure, so that the only advantage of nitric acid for this purpose is its comparative cheapness

Chromic acid gives a better yield of camphor than nitric acid, but here again it is possible to over oxidise, some camphoric acid being produced. The reagent is usually prepared by mixing sodium dichromate solution and sulphuric acid in such proportion that on reduction a solution of normal or basic chromium sulphate remains. Oxidation takes place readily at 50°–60°, the mixture being vigorously stirred in lead lined vessels. A solvent such as toluene is usually employed so that the product is a solution of camphor in toluene which at the saturation point contains approximately 70% of camphor

Consumption of dichromate is high and may be 50% in excess of the theoretical quantity, a figure which may be reduced by preliminary purification of the *iso*borneol, oxidation of impurities accounting for a relatively high proportion of the chromic acid.

$$3C_{10}H_{17}OH + Na_2Cr_2O_7 + 4H_2SO_4$$
$$\rightarrow 3C_{10}H_{16}O + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

As chromic acid in any form is an expensive reagent it is necessary to utilise the by-product of chromium sulphate. A limited market exists for basic chromium sulphate in the tanning industry, or for chrome alum if potassium dichromate is used instead of the sodium compound. But the quantity of chromium sulphate turned out by a large camphor factory would be many times the capacity of the market, and it is therefore necessary to regenerate the chromic acid, usually by an electrolytic process, although in countries not provided with cheap power the electric power consumption is a large item of cost.

As an alternative to the usual methods of oxidation, catalytic oxidation or dehydrogenation methods have been developed. Air in presence of active carbon or other catalysts at high temperatures oxidises *iso*borneol to camphor, but the conversion is not complete Catalytic dehydrogenation in presence of reduced copper was put forward in 1906 (B.P. 17573), and since that time other patents have claimed modification of catalysts usually based on copper or nickel. A process using reduced nickel has been described by O.

Aschan ("Naphtenverbindungen, Terpene und Campherarten," pp. 168–173). One difficulty with *iso*borneol is its tendency to revert to camphene, and certain catalysts promote simultaneous dehydrogenation and dehydration :

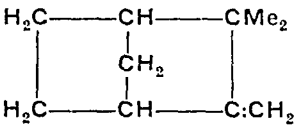
$$C_{10}H_{17}OH \rightarrow C_{10}H_{16}O + H_2$$
$$C_{10}H_{17}OH \rightarrow C_{10}H_{16} + H_2O$$

In some circumstances the dehydration reaction takes place almost exclusively, and this has given rise to the erroneous statement that *iso*borneol cannot be dehydrogenated by metallic catalysts.

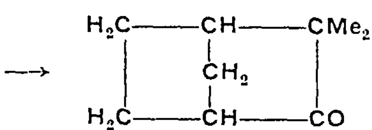
The dehydrogenation process is reversible and under suitable conditions camphor may be catalytically hydrogenated to a mixture of borneol and *iso*borneol. In order to obtain the highest conversion of *iso*borneol into camphor it is necessary therefore, to ensure separation of the hydrogen generated, or to carry the reaction out in several successive stages.

Borneol oxidises more readily than *iso*borneol, and as it is less readily dehydrated is more suitable for the dehydrogenation process.

Oxidation of Camphene.—It is possible to avoid the processes for converting camphene to *iso*borneol and thence to camphor by oxidation of camphene with chromic acid, a reaction first discovered by Berthelot (Compt. rend. 1869, 68, 334). The method is similar to the oxidation of *iso*borneol, but higher temperatures are necessary and yields are generally lower. Oxidation is facilitated by the use of acetic acid as a solvent. The formation of camphor by oxidation of camphene is explained by the intermediate formation of a compound of camphene and chromic acid followed by a Wagner rearrangement, direct oxidation of camphene, as for instance when alkaline permanganate is used, leading to the formation of camphenilone and other substances.



Camphene.



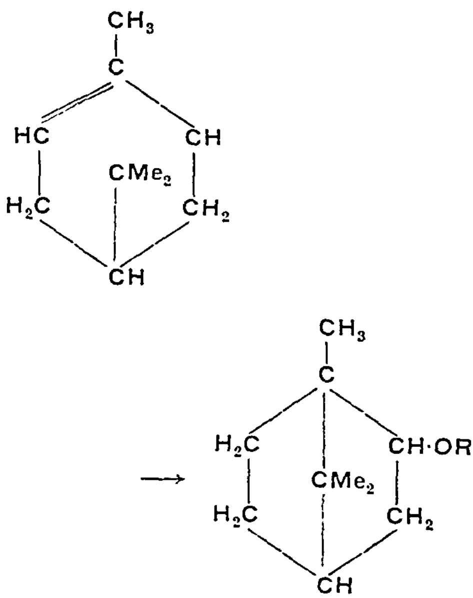
Camphenilone.

Evidence for the existence of a chromic acid compound has been obtained by Aschan (*op. cit.*, p. 166); it should be noted that camphor prepared by direct oxidation of camphene usually contains measurable quantities of *iso*borneol. In spite of the additional complications, however, it is generally preferred to go through the *iso*borneol stage, as higher yields are obtainable, and, if a catalytic oxidation process is used, the expense of chromic acid regeneration is avoided.

Refining of Camphor.—If an acid oxidising agent has been used, a preliminary treatment with caustic soda is necessary. Other methods comprise heating at a temperature of about 200° (B.P. 118489) with or without addition of alkaline reagents such as quicklime. These may be followed by sublimation, steam distillation, or dry distillation.

Sublimation is the oldest method of purifying camphor, and synthetic camphor may be treated in the same way as natural camphor. Objections to the sublimation process are based on the slowness of the operations and the large amount of space taken up by the sublimation chambers. Steam distillation gives a good product, but the consumption of steam is very high and the camphor has to be subsequently freed from water. Camphor also tends to adhere to the cooling surfaces and reduces their efficiency, and, owing to its high melting-point, there is a danger of blocking up. Some of these objections are overcome by distillation in a solvent such as light petroleum or benzene. Subsequently the solvent is removed from the camphor by vacuum distillation. Distillation may be carried out from an oil-jacketed vessel, preferably in presence of a solvent from which the camphor is afterwards crystallised.

Direct Pinene Esterification.—Pinene reacts with acids to give esters of borneol, but whereas the bornyl esters of weak acids give borneol on hydrolysis with alkalis, the esters of strong acids such as bornyl chloride are hydrolysed with greater difficulty and yield principally camphene and camphene hydrate. This is true not only of bornyl chloride ; a similar reaction has been investigated by Meerwein and collaborators (Annalen, 1927, 453, 16) who showed that 2-chlorocymene-5-sulphonic acid gave a 73% yield of the bornyl ester with pinene and that hydrolysis of the ester proceeded as for bornyl chloride. Weak acids, however, give low yields of bornyl esters from pinene, thus nullifying the advantage gained by the simplification of the manufacture as a whole.



Treatment of pinene with acetic acid by Bertram and Walbaum's process yields only a small proportion of bornyl acetate, together with fenchyl acetate, terpinyl acetate, and dipentene. A better yield is given by oxalic acid, and the manufacture of camphor was started using this process in America, but was not a success and the project was abandoned. Among other acids put forward are benzoic acid, salicylic acid, picric acid, tetrachlorophthalic acid, benzoyl benzoic acid, and boroacetic acid. Tetrachlorophthalic acid is claimed to give a high yield of bornyl ester but is rather an expensive substance, and, like benzoyl benzoic acid, is not stable in presence of alkalis. Boroacetic acid as a catalyst for the esterification of pinene by acetic acid has been proposed, and an investigation of the reaction has been carried out by Dupont and Pascaud (Bull. Inst. Pin, 1926, 437), who obtained 22–28% secondary alcohols (borneol and fenchol), 12–30% tertiary alcohols (terpineols), and the balance monocyclic terpenes.

By hydrolysis of the esters borneol is formed and not *iso*borneol; it is optically active, *l*-pinene giving *l*-borneol and by oxidation *l*-camphor. (Active *iso*borneol gives camphor of opposite sign.) The production of borneol is an advantage as it is more readily dehydrogenated; but on the other hand separation of the borneol is more difficult owing to the presence of fenchyl alcohol in considerable proportions. A mixture of fenchyl alcohol and borneol may be oxidised to the corresponding ketones and separation more readily effected by fractional distillation, fenchone distilling at 192°, compared with 209° for camphor.

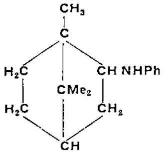
Pinene Isomerisation.—Direct conversion of pinene to camphene by catalysis was first observed by Armstrong and Tilden (Ber. 1879, **12**, 1752), who treated pinene with concentrated sulphuric acid, but the yield was very low. The action of clays on pinene first proposed in 1910 (B.P. 10227, 1910) was investigated by Gurvitsch (J. Russ. Phys. Chem. Soc. 1915, **47**, 877), who obtained evidence of camphene formation by this reaction. More recently Kuwata (J. Faculty Eng. Tokyo Univ. 1929, **18**, 117) and Rudakov and Tischtschenko (J. Appl. Chem. Russia, 1933, **6**, 691) have studied the reaction, yields of 56–62% camphene being claimed by the latter.

Other groups of catalysts have recently been patented. In G.P. 601236 various neutral sulphates, such as nickel sulphate monohydrate, are claimed. Another series includes weak inorganic acids such as antimonic, arsenic, titanic and tungstic acids, as well as complex heteropoly acids such as phosphomolybdic acid (G.P. 610402); in this patent a yield of 85% is claimed. In addition there are patents describing various methods of preparing the catalysts in an active form (*e.g.* F.P. 739770). The action of catalysts in the isomerisation of pinene to camphene is thus well established, but the mechanism of the reaction is obscure, no direct method of conversion being apparent from study of the structural formulæ of the two substances. In practice, the success of this process depends on the yield of camphene compared with the pinene hydrochloride process.

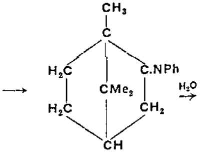
Ritter's Process.—This is described in J. Amer. Chem. Soc. 1933, **55**, 3322, although up to the present it has not been developed on a manufacturing scale. It forms an alternative route to camphor from bornyl chloride, depending on the reversible formation of phenyl *iso*bornylamine (*iso*bornylaniline) from camphene and aniline. The compound was first discovered by Ullmann and Schmid (Ber. 1910, **43**, 3202) as a by-product in the dehydrochlorination of bornyl chloride by means of aniline, and its formation is catalysed by aniline hydrochloride produced in the dehydrochlorination process. As the amine is of low volatility it can be readily separated from camphene, and by suitably choosing the concentration of the reagents and returning unchanged camphene after separation to the next batch, the whole of the camphene is finally converted to phenyl *iso*bornylamine, a substance which can be distilled at low pressures:

$$C_{10}H_{17}Cl + NH_2Ph \rightarrow C_{10}H_{16} + PhNH_2\ HCl$$
$$C_{10}H_{16} + NH_2Ph \rightarrow C_{10}H_{17}\ NHPh$$

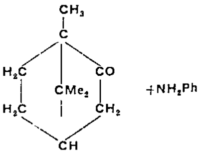
The secondary amine can be dehydrogenated to produce camphoranil in good yield. Dehydrogenation is best brought about by means of sulphur; metallic catalysts can also be used but are not so effective.



Phenylbornylamine (bornylaniline)



Camphoranil



Camphoranil, on hydrolysis with dilute sulphuric acid, gives a quantitative yield of camphor and aniline sulphate, from which aniline can be recovered for use again in the first stage of the process. This process gives camphor of good quality but has no special advantages for large-scale work over the more usual methods. No substantial improvement in yield may be expected since the largest loss takes place in the formation of bornyl chloride, which is common to both processes. Further considerations are the use of large quantities of aniline, and the production of sulphuretted hydrogen as a by-product.

Other methods of making camphor from pinene have been proposed, but although frequently quoted are at present of little value.

Any process for preparing synthetic camphor which can be made to compete with the cost of the natural product must obviously be a cheap process. Formerly the trees were cut down before the camphor was extracted from them, and as these trees were of some ten years' growth camphor prepared in this way was a costly material. In earlier days it looked as if the synthetic substance would replace that from the camphor tree and that the history of natural Indigo would be repeated. But the Japanese were wiser than the Indigo planters. They called chemistry and botany to their aid, and by improving the variety of plant and merely harvesting the twigs and leaves they were able to produce the natural ketone at a cost which rendered competition from the synthetic material exceedingly difficult.

Alternative Sources of Raw Materials.—Camphor has also been made from naturally occurring borneol or bornyl acetate. Borneol found in the Borneo camphor tree (*Dryobalanops aromatica*) in a crystalline state is scarce and is valued too highly for use as a raw material for camphor manufacture. Borneol is also found to a small extent (2–5%) in pine oil, many million pounds of which are manufactured annually. The expense of separating the borneol, however, has hitherto prevented development of this source of supply. Pine needle oil from the Siberian fir contains 33–40% bornyl acetate, together with smaller quantities of pinene and camphene. It is comparatively easy to separate the borneol and convert it to camphor by one of the usual methods, but apart from its value in perfumery, pine needle oil is limited and uncertain in supply besides being a monopoly of the U.S.S.R., so that at the present time it cannot be regarded as a potential source of camphor except, perhaps, in its country of origin.

Purification for Pharmaceutical Use.—Technical synthetic camphor is usually supplied as a white crystalline powder containing 90–95% camphor, together with *iso*fenchone, *iso*borneol, and bornyl chloride as the chief impurities. The melting-point is 150°–165° and affords a sharp indication of the state of purity owing to the high molecular depression of camphor, the pure compound melting at 178·0°–178·5°. Melting-point, however, is not entirely reliable, as some substances, including *iso*borneol, raise the melting-point of camphor even when present in low proportions. Purification of camphor is rendered extremely difficult owing to the closeness of the boiling-points of the impurities, all within a few degrees of 209°, which prevent ready fractional distillation, and also by the formation of solid solutions which interfere with the usual recrystallisation methods. A single recrystallisation alters only slightly the proportion of impurities; and *iso*borneol, having a lower solubility than camphor in the usual solvents, becomes concentrated in the solid phase, successive recrystallisations actually increasing the proportion of *iso*borneol. Methods have been found to overcome these difficulties and pure synthetic camphor is now available as an article of commerce, and is admitted to the Pharmacopœias of Great Britain, U.S.A., and Germany as an alternative to natural camphor, with which it is chemically identical, differing only in optical activity.

Purification for Use in Industry.—The technical grade of synthetic camphor is sufficiently pure for use in celluloid manufacture, although some impurities are more objectionable than others. Bornyl chloride should be eliminated as far as possible, but if the camphor is made by a process involving pinene hydrochloride, chlorine can usually be detected in the finished product, although this rarely exceeds 0·01%. *iso*Borneol is present to the extent of 2–4% and although having no positive value in celluloid is not specifically detrimental. *iso*Fenchone, on the other hand, has a gelatinising effect on nitrocellulose similar to that of camphor, and the chief objections to its presence are its lower stability to light and heat, and more pronounced odour.

Analysis.—Analysis of camphor cannot be carried out with great accuracy as there is no satisfactory method known for its direct estimation. Such methods as have been described depend on the reaction of semicarbazide, thiosemicarbazide, phenylhydrazine, hydroxylamine, etc., with the ketone group in the normal manner, and are not specific to camphor but take place also with other ketones, such as *iso*fenchone, which may be present. Owing to the different solubilities of the camphor and *iso*fenchone derivatives, gravimetric methods do not give a very accurate result for the total ketone content, although by using a system of solubility corrections a fair approximation can be obtained. A volumetric method using hydroxylamine hydrochloride gives good results for the total ketone content (Vandoni and Desseigne, Bull. Soc. chim. 1935, [v], 2, 1685).

*iso*Borneol can be readily determined by acetylation with acetic anhydride, followed by hydrolysis of the ester produced with standard alcoholic alkali. Chlorine is determined by oxidation with nitric acid in presence of silver nitrate, or by Stepanoff's method using sodium. A method using sodium peroxide is described in the U.S. Pharmacopœia, but there is no chlorine test in the corresponding B.P.C. 1934.

Plant used for synthetic camphor manufacture.—This calls for no special comment, and is constructed from the usual types of

apparatus or includes highly specialised units developed by the manufacturers concerned. The type of process adopted depends on the costs of raw materials and services; a process run by a highly organised chemical industry would preferably give the highest possible yield at the expense of an increase in complexity, whereas under more primitive conditions with very cheap pinene available, a simpler process giving lower yields might conceivably be more economical.

World Production and Prospects.—Official statistics for camphor relate only to imports and exports, and only very approximate estimates can be given for the total production, but it is probable that the world's annual camphor production is about 10,000 tons in normal conditions. This is divided among the principal producers as follows:

Natural Camphor (Japanese)	3,000 tons.
Synthetic Camphor (Germany)	5,000 „
„ „ (U.S.A.) .	1,000 „

About 80% of the world's camphor is used in celluloid manufacture and the remainder chiefly for pharmaceutical purposes. In India, an important market, the principal use is in connection with religious ceremonies and burning ghats.

During the economic depression of 1930–1935 camphor production fell considerably and has not yet (1938) reached the 1929 level. Any increase is unlikely to be large and there is not much scope for further expansion in the industry, the potential capacity of existing plants being in excess of normal requirements. Future developments will show an increased efficiency in manufacture with a preference for catalytic processes.

Prices of camphor at one time followed the price movements of natural camphor and were subject to wide variation. With the growth of the synthetic camphor industry the reverse has been the case, and natural camphor prices now follow synthetic camphor prices, which in the long run depend on the price of turpentine. Prices up to 7*s* 6*d* a lb. were recorded during the Russo-Japanese War of 1904–1906, and during the Great War, 1914–1918, but in the period 1930–1935 the lowest figure on record was a little over 1*s* a lb.

No attempt has been made in this article to give complete references to the subject, which are to be found principally in the patent literature. The following publications are available for further reference.

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CAMPHORONE. The ketone,

$$\begin{array}{c} CH_2\text{—}CHMe \\ \quad\ | \\ \quad\ CO \\ \quad\ | \\ CH_2\text{—}C\,CMe_2 \end{array}$$

obtained by the distillation of calcium camphorate, b.p. 200°–202°, d^{20} 0.933, n_D^{20} 1.4824 (Wallach and Collmann, Annalen, 1904, 331, 320).

CAMWOOD. Camwood, or "cambe wood," stated to be derived from a variety of *Baphia nitida*, Lodd. (*cf.* BARWOOD), is very similar in general properties to the other "insoluble red" dye woods. It yields, however, deeper shades on dyeing, and its colouring matter is said to be more soluble than that present in the other woods.

It has been examined by O'Neill and Perkin (J.C.S. 1918, 113, 126) who employed for this purpose similar methods to those found serviceable with sanderswood.

*iso*Santalin, $C_{22}H_{16}O_6(OCH_3)_2$, the main colouring matter, forms a chocolate coloured powder which on grinding becomes redder in appearance, and is readily soluble in boiling methylated spirit. When heated it shows no sign of melting, darkens at 280°, and is fully decomposed at 290°–300°, being then a carbonaceous powder. It gives with alcoholic potassium acetate the salt, $C_{96}H_{87}O_{32}K$ or $C_{72}H_{65}O_{24}K$, shows evidence of the formation of soluble oxonium salts, and in general properties closely resembles its isomer santalin. The colour reactions and also the dyeing properties of the two compounds indicate, however, that they are distinct substances. *Acetyliso-santalin*, $C_{24}H_{18}O_8(C_2H_3O)_4$, consists of a deep salmon pink powder which is gradually decomposed, without melting, between 250° and 280°. A molecular weight determination employing naphthalene gave the high figure 2,344, a result very similar to that given in these circumstances by acetylsantalin itself, and which may possibly be due to the production of a colloidal solution.

Deoxyisosantalin, $C_{22}H_{18}O_5(OCH_3)_2$, corresponding to the deoxysantalin of sanderswood, is a scarlet amorphous powder which, when heated, does not show a distinct melting-point but decomposes at 160°–165° with evolution of gas. A comparison of its colour reactions and dyeing properties with those of deoxysantalin shows that the substances are distinct. *Acetyldeoxyisosantalin*, $C_{24}H_{20}O_7(C_2H_3O)_4$, consists of an almost colourless powder which fuses and decomposes at 170°–175°. A molecular weight determination, employing naphthalene as solvent, gave the figure 1,324, which is approximately half that found in the same circumstances for acetyl*iso*santalin.

Camwood does not appear to contain either pterocarpin or homopterocarpin.

Dyeing Properties.—On wool mordanted with bichrome and cream of tartar *iso*santalin gives a violet-red, and deoxy*iso*santalin a dull red-violet shade. With santalin and deoxysantalin, under similar conditions, pale reddish-pink and dull crimson shades, respectively, are obtained. A. G. P. and E. J. C.

CANADA BALSAM (AND RESIN). Canada balsam is the oleo-resin exuding from schizogenous ducts in the wood of *Abies balsamea* Mill. (Fam. Pinaceæ) into cavities, from which it is collected. The tree is indigenous to Canada and the northern portion of the United States, the balsam being collected principally in Quebec. It is a clear, pale yellow, viscous substance, resembling turpentine oleo-resin. Its use is not extensive, being employed to a small extent in the manufacture of flexible collodion, and for the mounting of microscopic specimens, as it dries in a transparent form without crystallisation, and has a suitable refractive index. It often has a slight green fluorescence. The characters of Canada balsam are as follows:

Specific gravity at 15·5°	0·985–0·997
Optical rotation, a_D^{20}	+1° to +5°
Refractive index, n_D^{20}	1·518–1·523
Acid value	80–90
Ester value	4–8
Acid value of resin	120–125

The balsam contains from 15 to 25% of essential oil, having properties very similar to those of oil of turpentine, the chief constituent of the oil is *l*-pinene.

The resin is said to contain a resene and two acids termed α- and β-canadolinic acid.

According to Trost (Annali Chim. Appl. 1936, **26**, 38), the principal acid is *canadolic acid*, $C_{20}H_{30}O_2$, melting at 165°–168°, an isomer of abietic acid (*q.v.*). It is dehydrogenated (Se) to retene, gives a compound, m.p. 226°, with maleic anhydride, and is converted by acetic acid at 100° into Steele's abietic acid. E. J. P.

CANADA PITCH. Hemlock spruce resin. A reddish-brown resin resembling Burgundy pitch, exudes from the trunk of the hemlock spruce. *Tsuga canadensis* Carr. (Fam. Pinaceæ). It is used as an astringent in catarrhal diseases of the mucous membrane (B.P.C. 1934).

"CANADA SNAKE-ROOT" *v.* Asarum Canadense.

CANADINE, *one of the Hydrastis Alkaloids.*

CANANGA, ESSENTIAL OIL OF. The oil distilled from the flowers of *Cananga odorata* Hook (Fam. Anonaceæ), which is cultivated in the Philippine Islands, Réunion, Java, Madagascar, Mayotte, Mauritius, Jamaica, and the Seychelles. This tree is the source of oil of ylang-ylang, the finest qualities of which are produced in the Philippines and Réunion. The cananga oil produced in Java is of an inferior quality.

Composition.—The oil consists mainly of terpenes and sesquiterpenes with a small quantity of esters of acetic and benzoic acids, linalool, nerol, and farnesol.

Characters.—Sp.gr. at 15·5° 0·905–0·940, optical rotation at 20° −17° to −55°, n_D^{20} 1·490–1·505, ester value 10–40, ester value after acetylation 45–100. The oil is not soluble in 90% alcohol, and even in 95% alcohol it forms a slightly opalescent solution. C. T. B.

CANARIN. When a solution of ammonium sulphocyanide and sodium chlorate is boiled, a yellow precipitate of persulphocyanogen $C_3H_3HS_3$ ["Canarin," Prochoroff of Moscow] is formed. This reaction is readily carried out on the fibre, and affords a cheap method for the production of a fast yellow. As there is a tendency to weaken the fibre, particularly when in contact with hot metal, traces of a vanadium salt are added (H. Schmid, J. Soc. Dyers and Col. 1921, **37**, 219).

CANAVANINE *v.* Amino Acids.

CANDELILLA WAX is the commercial name given to a deposit that forms on the twigs and leaves of the candelilla tree, of which there are several species, *Euphorbia antisyphilitica*, *Pedilanthus pavonis*, and *P. aphyllus*, all belonging to the Euphorbiaceæ, and growing in Texas, Arizona, Mexico, and the northern parts of Central America.

Originally the wax was separated from the plant by means of steam, the yield being 1·5–2·5%, but it is now usually extracted with solvents, notably benzene, and a yield up to 6% is obtained. Special forms of extractor were patented by Thatcher (U.S.P. 1056378, 1913), and a method and apparatus for crushing, screening, and extracting the plant were claimed by Garcia (U.S.P. 1715194, 1929). Other methods of extraction include that of Sharp (U.S.P. 1018589, 1912), in which the plant material is mixed with fullers' earth and extracted with light petroleum, and those of Watson (U.S.P. 1042992, 1912; 1058648, 1913), in which the material is heated to 149° and subjected to a downward current of steam.

The crude wax is yellowish-grey to dark brown and at the ordinary temperature is odourless, but when warmed has a fragrant aromatic odour. It is refined by melting with water acidified with sulphuric acid and straining, or by treatment with solvents and adsorbents. In the process claimed by A. Riebeck'sche Montanwerke A.-G. (B.P. 299357, 1928) the crude wax is dissolved in methyl alcohol, glycol, butanone, or other solvent, and treated with an adsorbent, notably decolorising carbon activated with zinc chloride.

The crude wax may contain from 1 to 6% of water, and this is the probable explanation of the high specific gravity recorded for some specimens (*e.g.* by Farcy, Ann. Falsif. 1920, **13**, 97); it may also contain as much as 15% of dirt including about 1·5% of mineral matter.

Govier (Oil and Fat Ind. 1930, 379) gives the following values for commercial samples of the wax:

	Sp.gr. at 15°.	Melting-point.	Acid value.	Saponification value.
Light wax	0·993	68·4	21	55
Dark wax	0·950–0·990	68–70	13–18	50–60

Values recorded for the crude wax are as follows:

Specific gravity at 15°	0·9825–0·9850
Acid value	12·4–14·4
Melting-point	67°–71°
Solidifying point	64°–68°
Saponification value	46·1–64·9
Iodine value	16·6–36·8
Unsaponifiable matter	77–91%
n_D^{70}	1·4558

The variations in the melting point, acid value, and iodine value are attributable to the different amounts of resin (Meyer and Sojka, Monatsh. 1913, 34, 1159).

Farcy (*l c.*) obtained about 6% of wax from *Pedilanthus aphyllus* by extraction with benzene. It had the following characteristics :

Melting point	. 64°–66°
Specific gravity	1 001–1 002
Free acids	18–19%
Total acids . . .	. 66–67%
Hydrocarbons	33%
Iodine value .	20–21

According to Staempli (Seifens Ztg 1931, 58, 55) candelilla wax contains from 50 to 52% of hydrocarbons, especially hentriacontane, $C_{31}H_{64}$ (m p. 68°), about 1% of a hydrocarbon of m p 85°, 20% of melissic acid partly free and partly as the myricyl ester (m p. 88°–90°), 10–14% of myricyl alcohol, 10% of resinous constituents and traces of a phytosterol with m.p. over 150°.

Collins (J S C I. 1935, 54, 33T) found 70% of a hydrocarbon similar to that in esparto wax (Meyer and Soyka, *l.c*) consisting mainly of the *n* paraffin, $C_{31}H_{64}$, melting at 62°–63° (undef), with a second well defined m p. 67 7°–67 8°, and resolidifying at 67 4°.

Leys (J. Pharm. Chim 1925, 117, 417) devised a method of analysing candelilla wax and similar vegetable waxes, according to which the saturated acids are separated in the form of copper salts and the higher alcohols by means of benzene.

The colour of the wax, which is not readily bleached, is a drawback to its use for many purposes for which carnauba wax is suitable.

It is used in the manufacture of gramophone records, boot polishes, linoleum, varnishes, and carbon duplicating papers, and for the insulation of telephone wires. C. A. M.

CANDLENUT. (*Aleurites triloba* Forst. or *A. moluccana*, Wild) This is a tropical oil-bearing nut of similar size and shape to the walnut. The nuts are eaten, roasted, by natives. The oil itself is unsuitable for food owing to its purgative properties. To separate nuts from the shells after crushing a process of flotation in brine (d 1·10) is adopted. P. Amann (Recherches et Inventions, 1935, 16, 312) records analyses of Madagascar samples as follows .

Percentages :

	Shells	Kernels
H_2O . .	7 97–9 86	3 14–3 49
Crude protein .	1 72–2 19	18 75–24 56
Ether extract . .	—	61 6–65 5
Ash	4 04–7 74	2 76–3 34

Constituents of Ash :

P_2O_5	0 93–1 88	20 5–28 3
K_2O	1 95–3 79	5 86–7 46
CaO	32 6–60 6	5 4–7 8
MgO.	2 25–3 50	0 82–1·77

A. G. Po

CANDLENUT OIL or LUMBANG OIL is the fatty oil obtained from the seed kernels of the tree *Aleurites moluccana* L., Willd. (= *A. triloba* Forst.[1]) (Fam Euphorbiaceæ), which is a native of the South Sea Islands of the Malayan region, Polynesia and the Hawaiian Islands The tree is especially cultivated for the sake of the oil in the Philippine Islands, both for local and export purposes, and has also been introduced into Madagascar, Africa and Brazil. The English name "candlenut" is stated to be derived from the practice of the Hawaiians of stringing the dried kernels on to reeds or sticks in order to form a "candle," several of which are wrapped in a pandanus leaf in order to make a torch (*cf.* E. V. Wilcox and A. R. Thompson, Hawaii Agric. Exp. Stat. Bull 1913, 39) In the Philippines the tree is known as "lumbang" or "lumbang bato," and in Brazil as "nogueira de Iguape" ; to the French it is known as "bancoulier" and to the Germans as "Bankulnussbaum," "Candlenussbaum" or "Lichtnussbaum" ; the oil is also known as "kekui," "kukui," or "Kekuna" oil in Hawaii and Ceylon.

The seeds, often erroneously termed "nuts," have very hard shells, and, moreover, it is difficult to separate the kernels from the shells . the natives either break the seeds by hand-labour or employ methods by which the seeds are first heated and then rapidly cooled in order to fracture the shell and allow the kernels to be extracted , for large scale production it may prove practicable to separate shells and kernels by sifting after a short crushing treatment of the dried seeds in an edge runner mill (Georgi, Malay. Agric. J. 1926, 14, 292) The kernels contain from 50–60% of oil, corresponding to 16–20% on the whole "nut." The cold drawn oil is limpid and pale in colour ; the statement that cold drawn lumbang oil from plantations in Florida is fit for edible purposes (Gardner, Amer. Paint and Varnish Manuf. Assoc., Circ. 335, p. 611) requires confirmation, in view of the fact that the Philippine oil, at least, contains an essential oil (Santiago and West, Philippine J. Sci. 1927, 32, 41) and has usually been credited with purging properties. The expressed cake is unsuitable for use as a cattle food owing to its purging and toxic properties. (For analyses of kernels and cake, *see* Semler, "Die Tropische Agrikultur," 1913, II, 515 ; Aguilar, Philippine J. Sci. 1919, 14, 275; Lewkowitsch, J S C I. 1901, 20, 909). The expressed oil has the following characters : sp gr. at 15° 0 920–0 929, refractive index 1·4724–1 476/30°, saponification value 188–214 (usually 192–195), iodine value 140–164 (usually 149–160), unsaponifiable matter 0 3–0 4% (*see* Richmond and del Rosario, Philippine J. Sci 1907, 2A, 439 ; West and Montes, *ibid.* 1921, 18, 619 ; Eaton, Agric. Bull. F.M S 1919, 7, 162 ; Georgi, Malay. Agric. J. 1922, 10, 202 ; 1926, 14, 292 ; T. H. Barry, J.S C.I. 1929, 48, 289T ; Glaze, Chem. Met. Eng. 1927, 34, 749).

The fatty acids from samples of the oil examined by Walker and Warburton (Analyst, 1902, 27, 237) yielded 11 2–12 6% of ether-

[1] *A triloba* has been occasionally, but erroneously, referred to in the literature as a distinct species, but all stages of leaf development, from simple leaf to the three-lobed type, may be found on the same tree (*cf* H Semler, "Die Tropische Agrikultur," 1903, II, 517)

insoluble hexabromides, corresponding to a content of about 4–4·6% of α-linolenic acid, whilst Cruz and West (Philippine J. Sci. 1930, 42, 251) report about 8% of α-linolenic acid. About 2% of saturated acids are present, and the balance of the acids consists of linolic and oleic acids. It will be noted that although the lumbang tree is allied botanically to the tung oil tree, *A. Fordii* Helmsley (*see* ALEURITES SPECIES), and to the "soft lumbang" ("bagilumbang" or "lumbang banaculag") *A. trisperma* Blanco, the seed-oils are strikingly dissimilar, since candlenut oil, unlike the others, contains no elæostearic acid. In correspondence with its low content of α-linolenic acid and high content of linolic acid, candlenut oil exhibits fair drying properties and is used in the tropics for the preparation of paints, etc., as well as for soap-making and as an illuminant. A more extended application to the manufacture of paints, printing inks, rubber-substitutes, soft soap, etc., would appear to be justified (see A. P. West and Smith, Philippine Bur. of Forestry, Bull. 1923, No. 24; Aguilar, Philippine J. Sci. 1917, 12, A, 235; T. H. Barry, *l.c.*). E. L.

CANDLES. A candle is a solid illuminant consisting of a rod of fatty or waxy combustible material surrounding a central wick. By means of the wick the melted wax is fed regularly, by capillary attraction, to the point of combustion at the tip of the wick.

The earliest forerunner of the candle was undoubtedly the torch, consisting of pine branches saturated, naturally or artificially, in resinous or fatty matter; but primitive forms of the wax candle and tallow dip (rush-light) were known to the Romans. From the earliest days the production of tallow candles was a house industry, for which domestic waste fat (tallow) was used, whilst the more expensive beeswax was utilised for the wax lights employed by the richer classes and for religious purposes (*v. infra*). This distinction is emphasised by the different nomenclature applied by the Romans (*sebaceus* and *cereus*) and the French (*chandelle* and *bougie*) to tallow and beeswax candles respectively; there is also an essential difference in the method of manufacture, tallow candles being dipped and beeswax candles being poured (or drawn) and rolled, which is reflected in the existence of two distinct Livery companies in the City of London, viz. the Tallow Chandlers and the Wax Chandlers.

Spermaceti, a white crystalline wax constituting the solid fraction of sperm oil, from the head-cavity of the sperm whale or cachalot, came into use in the middle of the eighteenth century; it is now used only to a limited extent in candle manufacture, in admixture with other materials. Formerly the sperm (*i.e.* spermaceti) candle[1] was used as a photometric standard of light, but it has now been entirely superseded by the pentane lamp, electric lamps, and, more recently, by radiation standards.

[1] The modern so-called "sperm candle" is no longer made of spermaceti, but is composed of the ordinary mixture of paraffin wax and stearine: the name merely denotes a particular size and shape.

Tallow, as a candle material, suffers from the disadvantage that it emits an acrid odour on burning, due to the formation of acrolein by incomplete combustion of the glycerol present in the fat. An enormous improvement in candle manufacture was effected by the introduction of *stearine*, a mixture of palmitic and stearic acids, which followed as a result of the researches of M. E. Chevreul (1815: "Recherches chimiques sur les corps gras d'origine animale," 1823) on the saponification of fats and their successful technical exploitation by de Milly and Motard (1833: *cf.* Payen, Bull. Soc. d'Encour. 1833, 156); these fatty acids, which are prepared by the hydrolysis or saponification of the glycerides constituting natural fats, contain no glycerol and therefore produce no unpleasant smell during combustion. The melting-point of stearine is higher than that of tallow, and it is, moreover, excellently suited to the production of candles by moulding (casting), provided the manipulation is carefully conducted so as to prevent cracking during cooling (*v. infra*).

Stearine was in its turn displaced from its leading position by *paraffin wax*: in 1851, James Young (B.P. 13292, 1850) succeeded in producing a pure white paraffin wax from Scottish shale oil, which was applied to the manufacture of candles under a patent by J. K. Field and C. Humfrey (B.P. 454/1856; *cf.* J. L. Field and C. Humfrey, Jun., B.P. 1821/1857; *cf.* also earlier patents of G. F. Wilson. B.P. 12512/1849, and W. de la Rue, B.P. 1748/1853). The absence of any tendency to crack during cooling (which had caused difficulties with the early stearine candles), the lustre, and ready adaptability to ornament in shape and colour, of paraffin wax rapidly established the pre-eminence of this material for candle manufacture; moreover, it was soon available cheaply and in large quantities.

The most important materials for present-day candle manufacture (apart from *beeswax*, which is only used for special purposes, *v. infra*) are *stearine* and *paraffin wax*. Pure **stearine candles** are still produced in quantity on the Continent (especially in France, Belgium, Holland, and the Scandinavian countries), but in England, Germany, and the United States, they are only used to a relatively small extent for lamps and purposes where the opaque appearance and exceptional stability to heat are particularly valued. In these countries stearine is chiefly used in admixture (from 2–30%) with paraffin wax, in order to impart greater stiffness and opacity to the latter. Pure paraffin wax is unsuitable for use alone in most cases, as the readiness with which it liquefies by heat causes the candle to "gutter" excessively; moreover, paraffin wax has the objectionable property, which is independent of the melting-point, of becoming plastic after exposure to a moderate degree of heat, and so allowing the candle, unlike a stearine candle, to bend at temperatures considerably below its melting-point.

Candle stearines are chiefly obtained from tallow, palm oil, and bone fats. Either the Twitchell or the autoclave process may be

used for the saponification, and the crude acids are subsequently distilled before pressing out the liquid oleine. In the earlier days of stearine candles, the acid saponification process, which induced the formation of large amounts of solid unsaturated acids (*iso*-oleic acid) and so increased the yield of solid candle material, was favoured, but whilst *iso* oleic acid is a satisfactory constituent (within limits) in stearine candles, it *may be detrimental in mixed stearine paraffin* candles Hence such processes are now not much used, at least in this country, for the preparation of candle stearines The art of manufacture consists in so selecting the stock that the proportions of palmitic and stearic acids in the final distilled product will be such as to give suitably large crystals, from which the accompanying oleine may easily be expressed. The following figures illustrate the properties of a distilled saponification stearine of good quality for candle manufacture m p 130°–133°F. (54 4°–56 1°C.), acid value 207–208, saponification value 208–209, iodine value 1–6, neutral material less than 1%, unsaponifiable matter practically nil, mean molecular weight of the acids 268–270 Such a "stearine" *consists of a mixture of palmitic (about 53 5%)* and stearic acids with a small proportion of oleic and *iso* oleic acids, hydroxystearic acid, etc. Similar standards have been adopted by the American manufacturers. (For specifications and methods of testing prescribed by the French War Dept. for stearine candles, *see* P Bruère, Ann Falsif 1933, 26, 70) In order to obtain satisfactory burning, it is essential that the ash content—and in particular the lime content—should be a minimum, as even traces of lime (of the order of 0 003%) are stated to cause the formation of a "skeleton" on the wick and consequent guttering (*cf.* Graefe, Seifens.-Ztg. 1907, 34, 1107) In recent years, considerable amounts of pale "stearines" made from hydrogenated fish oils and known in Japan as *stearine rō*, have appeared on the market (*cf.* Godo Yusi Glycerin K K, Jap P 93856; Ueno and Tschuchikawa, J Soc Chem Ind. Japan, 1935, 38, 693B); this product contains some undesirable low melting acids A neutral solid wax, known as *kokaro*, prepared by the hydrogenation of sperm body oil, is also available; this product does not give either the same opacity or stability to a mixed candle as do ordinary stearines, but as both these products can be produced cheaply in Japan, they are able to compete there with paraffin wax (*cf.* Allan, J. Inst. Pet. Tech. 1933, 19, 155).

Coconut stearin, which is a neutral material consisting of coconut *oil*, from which the more liquid constituents have been removed by expression (*cf.* Soames, B.P 5842/1829), was originally the chief ingredient of Price's "Patent Candle" and was retained for a long time as an important ingredient of night lights; it has now, however, been largely displaced in this country by paraffin wax compositions.

In the United Kingdom, paraffin wax from Scottish shale is used for candle manufacture, as well as petroleum paraffin waxes from the United States, Burma, Galicia, Assam and Borneo, in Germany, paraffin wax is manufactured locally by the distillation of brown coal or lignite. Commercial paraffin waxes may have melting-points ranging from 30°–56°C. (86°–133°F.); Rangoon petroleum yields harder waxes with melting points up to 140°F. As the harder waxes have a certain tendency to stick in the moulds, it is common practice to blend paraffin waxes in order to produce mixtures of *suitable properties (setting point 120°–138°F.)*

As already stated, a proportion of a suitable stearine is usually admixed with the paraffin wax as a stiffener in order to prevent bending of the candles, but the stability to heat of a mixed candle is never as great as that of pure stearine candles, further, the inclusion of stearine imparts to the otherwise translucent paraffin wax an attractive opaque appearance, which is regarded by the public as an indication of quality. Whereas formerly 20–30% of stearine was employed, much smaller proportions are now current, for the desirable appearance can be imitated by the addition of small amounts of "opacifiers" such as β naphthol or β naphthol benzoate ("Hertolan") Small amounts of other waxes, such as carnauba wax, *montan wax, and ceresin (purified ozokerite)* are occasionally employed as stiffeners in addition to, or in place of, stearine Additions of minor amounts of various materials, *e g* lead stearate (Burke, B P. 14975/1914), methyl or ethyl alcohol (Moietti, F.P. 431490/1911), amides (*e g p* phenylenediamide of stearic acid), etc., have from time to time been claimed to improve the appearance (by preventing "mottle") of the paraffin candle, or to facilitate moulding.

The Wick.—The proper preparation of the wick is a very important part of candle manufacture, since the behaviour of the candle in use largely depends upon its construction and treatment In the early prototypes of the candle, the amount of material serving as wick was large in comparison with the amount *of combustible material, for example*, the pine branches in torches, the rope-strands of the "link," the hempen cord of the "flambeau," and the rush-pith of the "rush lights," but this proportion has been gradually reduced, until the modern ratio of about 1 part of wick to 50 parts of combustible has been reached.

Until 1825 the only wicks used for "dips" or candles were made of rush-pith or of twisted flax or cotton yarn. As no means for consuming the wick evenly were available, the charred and smoking end hung down over the side of the candle and required periodic "snuffing" Cambacères, in 1825, was the first to recognise that the wick could not be consumed in its central position, and devised the "braided" or plaited wick, which exhibits a tendency to curve *over in one direction*, thus bending the glowing end of the wick over into the outside (oxidising) region of the flame, where there is sufficient oxygen to burn it completely. This work was followed by various inventions designed to improve upon the earlier form of the plaited wick, for example, by twisting the wick round a rod and coating one side with paste (W. Palmer, B.P. 9146/1841), or by introducing "gimping" strings of wire (Price's Co, 1840). One of the

most successful of these devices was the "metallic-wick candle" invented by Palmer (B.P. 14264/1852), who introduced a fine thread coated with metallic bismuth (the "doctor") into the wick: when the candle was lit, the fusible metal formed a small globule at the tip of the wick, which, by its weight, bent the wick over into the outside of the flame, where the charred cotton was oxidised and the bismuth volatilised. Cambacères' original wick was round, but the later flat type of wick (first made by Thomas Topham in England at Ripley in 1836) proved entirely satisfactory when properly "pickled" and is still in use to-day. The "pickling" process consists in impregnating the wick with a dilute solution of certain mineral salts, the effect of which is to produce clean burning by regulating combustion and helping to vitrify the ash: "pickling" also appears to be one of the secrets of the bending of the wick. Cambacères, in his original patent, recommended a bath of sulphuric acid, but better materials were soon introduced, such as boric acid (de Milly, 1836), bismuth nitrate (Palmer, B.P. 5979/1830), ammonium borate (d'Arcet). The modern pickling solutions are mostly prepared from selected mixtures of borax, ammonium chloride, sulphate or phosphate, potassium chloride or chlorate, sulphuric and nitric acids, nitrates, silicates or tungstates; almost every manufacturer has his own recipe, regarded as a trade secret, adapted to the wick and to the candle material employed. The proportion of the salt to water is usually about 2 oz. to 1 quart. The braided cotton yarn, cut into hanks of "wicking," is bleached and washed and then steeped in the "pickle" for about 24 hours, after which it is drained, and the residual water (which would reduce the capillarity) is removed in a high-speed centrifugal machine, which does not cause torsion or other disturbance in the threads; if necessary, further drying may take place in heated drying rooms. The amount of salt remaining in the fibre is, of course, small, but is sufficient materially to influence the burning of the candle. Few candle-makers plait their own wick, which is usually supplied in the required plaiting by the cotton spinners; as a rule it is plaited from three groups of an equal number of twisted cotton strands, and the success of the wick depends on the manner in which it is braided, the tightness of the plaiting, and the size of the wick. The relative tightness, in particular, depends on the candle-material to be employed; paraffin wax, which melts and travels easily, requires a thin, very tight wick; stearine takes a moderately tight wick, while beeswax and spermaceti, which are less mobile, require a thick, loosely braided wick. While flat wicks are used for paraffin and stearine candles, braided wicks of round section are preferred for beeswax candles. For tallow candles (tallow dips), and tapers, braiding is not necessary, and the old-fashioned twisted wick is always employed. The effects of the subsequent pickling must be considered in relation both to the braiding and to the candle material. The treated wick is wound from the circular frames on which it was dried on to "spools" or bobbins: the winder is of simple type and the task is performed by girls or boys, who let the wick run through their fingers as they wind, in order to detect any knots or other irregularities which might interfere with the proper burning of the candle. The spools are then ready for use.

The Candle.—Whilst the bulk of the modern candles—the paraffin wax and stearine candles—are produced by **moulding**, the older methods of **dipping** and **pouring** are still retained for the production of candles from tallow and beeswax respectively, as these materials cannot be moulded satisfactorily. The **drawing** process is applied to the manufacture of tapers and similar articles (*v. infra*).

Dipping is the cheapest, as well as the oldest, method of making candles, and has been a domestic method since at least the times of the

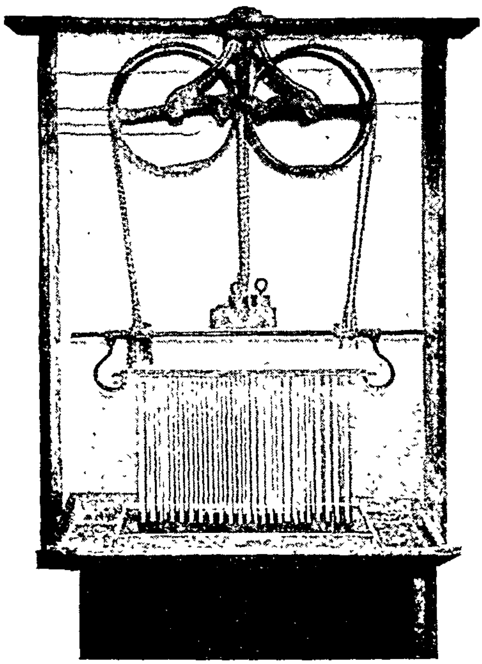


FIG. 1.

Romans: the harder portions of the household waste fat were melted down or rendered over salt water and strained, and the wicks—either rushes peeled so as to leave only a thin strip of peel to support the pith, or flax or cotton fibres—were alternately immersed ("dipped") in the melted fat and withdrawn to cool until a sufficiently thick coating of tallow was obtained, after which the *dips* were hung up to harden and whiten. The process requires a certain skill, and in mediæval Paris there was a guild of candlemakers whose members travelled from house to house to make tallow candles in this manner.

The large-scale manufacture of "dips" is merely an extension of this process. The twisted cotton wicks are strung on rods or "dippers," each of which holds from eight to twenty-four wicks, and these are supported on a frame

which is suitably suspended so that the rods and wicks can be raised or lowered as required by means of counterweights. Fig. 1 illustrates a simple form of such apparatus in current use [in a more elaborate machine, the counterpoised "dippers" are suspended from the circumference of a horizontal, revolving frame mounted on a central pillar, so that each set of wicks can readily be dipped in succession] As a rule, about four dippings are required to produce a candle of sufficient thickness

Pouring.—Formerly the larger sizes of beeswax church candles were made by "rolling" round a wick a cake of warm wax, which had been kneaded until it was plastic, but this method has been entirely superseded by the somewhat primitive process of "pouring," whereby the melted beeswax is poured over the wicks, which are suspended from a hoop-like frame (Fig 2) which can be rotated by hand For the larger sizes, the candles have to be reversed from time to time in order to ensure a uniform thickness The hoops are hung in a current of air after every two or three pourings.

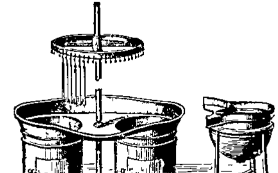


Fig 2

When the candles are of the requisite thickness, they are severed from the frame and skilfully rolled on a marble slab under a weighted board to smooth away any irregularities in the hands of an expert workman, the candles can assume the evenness of moulded candles, with a peculiar softness which is indescribable, but unmistakable when once identified. The ends are cut clean, and the tips are shaped by hand. In section, a well made beeswax candle shows a series of concentric rings corresponding with the successive pourings.

The pouring process involves much skilled labour the raw material itself is also expensive, and as beeswax candles offer no practical advantage as an illuminant, they are now only employed for ecclesiastical purposes, or, rarely, as a fancy article.

To adapt the beeswax as it comes from the comb to the requirements of the chandler, little is needed beyond ordinary cleansing by repeated melting in hot water; the wax may then be bleached by exposing it (in the form of thin ribbons) to light and air; if necessary, chemical bleaching with acid dichromate is adopted. In accordance with the requirements of the Roman Catholic Church, the principal liturgical candles must consist wholly or "for the larger part" of beeswax, the proportions for different candles being specified (cf Rescript of the Sacred Congregation of Rites, Dec. 14, 1904, Official Notification of their Lordships the Bishops of England and Wales, Dec. 4, 1906); in England, from 65 to 95% of beeswax is employed, but in the United States, the "larger part" is interpreted as a minimum of 51% (cf Power and Hauber, Ind Eng Chem. (Anal) 1932, 4, 389) Other candles used on the altar must contain at least 25% of beeswax.

The **drawing** process is applied to the manufacture of tapers, the waxed wicks for night lights, wax vestas, and candles of small diameter such as "birthday" or "Christmas tree" candles (the latter may also be made by moulding) For this purpose a long length (about 1,600 yards) of twisted cotton wick is repeatedly "drawn" through a bath of molten wax (mainly paraffin wax with various proportions of beeswax or stearine according to quality) by winding the wick in alternate directions from one large drum on to another In order to ensure an even thickness and smooth surface of each coating, the coated wick, as it leaves the bath, is drawn through a circular die, of which the diameter is increased at each traverse The operation is continued until the taper or cable has acquired the requisite thickness In a modern taper plant, as many as 24 strands may be drawn simultaneously, several steam heated baths of, for example, differently coloured wax being used. The final wax cable is cut into short lengths and the ends of the tapers are dipped into hot water and shaken, this process—known as "feathering"—removes the wax from the tip of the taper, leaving a tuft of clean cotton by which a new taper is easily lighted for the first time without dripping wax Night light wicks may be "feathered" by bruising the tips with a small mechanical hammer or stamper In Poland, candles are made by the drawing process, the ends being tipped by a machine (Allan, l c).

Moulding.—With the exception of small candles made by the drawing process, all stearine and paraffin wax candles are now made by a moulding or casting process. The introduction of moulds is attributed to a Sieur de Brez of Paris in the fifteenth century; but as the process was unsuitable for beeswax candles, and only moderately successful with the harder grades of tallow, little progress in design was made, until the introduction of spermaceti, and especially of stearine and paraffin wax, as candle materials opened a rich field for development.

The simplest form of moulding machine is the "hand-frame" (introduced by Freitag in 1724), which consists of a frame holding a number of vertical, tapered pewter moulds with the pointed ends downward, and the upper (butt) ends opening into a shallow trough: a wick is threaded longitudinally through each mould and held in position by suitable clips or pegs at each end The melted candle material is poured into the moulds, until the trough is full (to allow for contraction on cooling) and the frame is left to cool in the air, or plunged into

cold water: when cold, the superfluous wax is removed with a trowel, and the candles are removed by simply inverting the frame. These hand frames have been superseded by multiple moulding machines, except for odd sizes of candle, for which it would not be worth while to maintain a special machine.

The use of steam and water for the alternate heating and cooling of the moulds was introduced by Binns (B.P. 2488/1801). Further inventions and improvements by Morgan (B.P. 6610/1834), Tuck (B.P. 7409/1837), Palmer (B.P. 12077/1848), Cowper (B.P. 1988/1856), Humiston (B.P. 2541/1857, in the name of Newton), Stainthorp (B.P. 2556/1857, in the name of Pitman), Stainthorp (B.P. 740/1860) led by degrees to the modern continuous-wicking type of moulding machine such as is shown in Fig. 3.

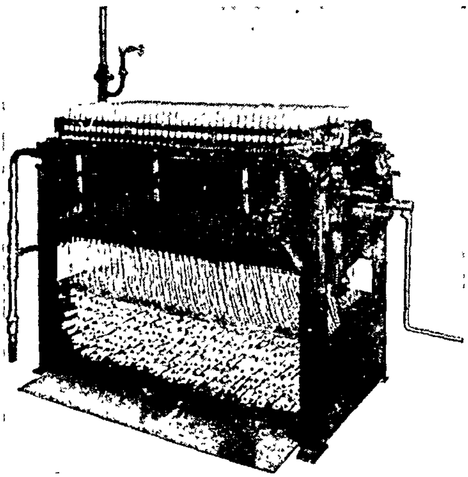


Fig. 3.

Such a machine consists essentially of a metal water-tank containing a large number of tubular moulds or pipes, which are slightly tapered to facilitate the ejection of the candles; the moulds, which are polished internally, are made of pewter or tempered tin (98% purity) and may be strengthened by an external sheath of hard-drawn brass or steel (porcelain moulds have been patented (G.P. 195702), but are too costly and have little, if any, advantage). The upper (butt-) ends of the moulds open into a shallow trough, and the lower ends are closed by the conical tip-moulds, which are perforated to allow the passage of the wick and carried on the upper end of hollow piston-rods which can slide up and down within the pipe. The pistons are coupled to a movable plate or "driving board," which can be moved up or down by means of a handle operating through a rack-and-pinion gear or a screw. Cold water and steam can be admitted to the tank as required. The wick-spools, which are equal in number to the number of moulds, are free to revolve on the pins at the bottom of the machine, and the wicks are threaded up through the piston-rods, tip-moulds, and candle-moulds: the arrangement is illustrated in the section in Fig. 4.

In older machines, as well as in many contemporary types, the spool pins are horizontal (*cf.* Fig. 6), but the vertical arrangement shown in Fig. 3 is claimed to reduce tangling and breaking of the threads.

Above the trough enclosing the butts of the moulds are the "clamps," which serve to hold the candles after ejection from the moulds. To begin casting operations, the wicks are threaded into the moulds and temporarily secured in the trough, or a few inches may be left loose in the moulds. The tank is filled with water, and steam is admitted until the moulds are heated to the requisite temperature. The molten wax is poured in to fill the moulds and the trough, and cold water is passed into the tank. When the candles have solidified, the trough is scraped clear with a "spud" (a blunt knife the width of the trough), and the candles are ejected from the moulds by manipulating the handle which raises the pistons and tip-moulds. As the candles pass upwards into the open clamps (which close on them when the candles have reached the proper height), they pull up fresh wick after them and hold it correctly centred in the moulds in preparation for the casting of the next batch of candles. The pistons are then wound down until the tips close the bottom of the moulds. The casting process is then repeated, this time, as on subsequent occasions, with all the precautions, correct temperatures, etc., applicable to the particular candle-material in question.[1]

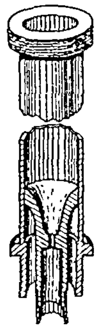


Fig. 4.

When the candles have solidified in the moulds, the wicks above are severed with a special knife; the rack of clamps holding the "dummies," or previous batch of candles, is removed and emptied, and replaced ready to receive the new candles as they are racked up, and the whole process is repeated as required.

The temperatures of the molten candle-wax, of the moulds before filling, and of the cooling water, depend upon atmospheric conditions and upon the nature of the candle-material in question. Pure stearine may crack if chilled too quickly, or crystallise and spoil the appearance of the candle if cooled too slowly: stearine, therefore, is cooled to a creamy consistency before it is poured into the moulds, which are finally cooled with tepid water, solidification of the candle taking about 25 minutes. For paraffin wax, however, the moulds are heated to nearly 200° F., and the wax to 170°–180° F., before filling, according to the setting-point of the wax employed, and the moulds may be cooled rapidly by running cold water into the tank: if properly carried out, the candles acquire a high lustre.

The refinement, known as the "self-fitting" butt, introduced by J. L. Field (B.P. 3032/1861,

[1] The candles or "dummies" of the first batch, in which the wick was not properly centred, merely serve to provide starting-points for the wicks and are discarded when they have served their purpose.

cf. Figs. 5, 7) makes it possible for the candle to be fitted into any reasonable sconce without scraping or additional packing.

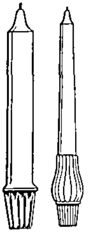


Fig. 5

As the self fitting butt is tapered, special arrangements are needed in order to allow for the ejection of the candles from the moulds. In the machine patented by E Cowles the self fitting ends are moulded separately by means of conical caps or butt moulds which fit into the tops of the main candle moulds and are removed by hand after winding up the candles into the clamps.

It will be obvious that this complication necessitates cutting the wicks each time in order to allow the butt moulds to be re-threaded on to the wicks for the next batch, a process which involves considerable labour and a waste of a certain amount of wick. Nevertheless, this type of machine is still preferred by some candle makers to Cowles' later and more elaborate continuous wicking machine in which split butt moulds, mounted in a divided bed plate, are employed, which open apart to allow

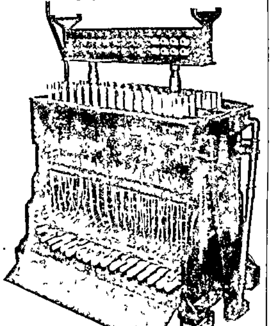


Fig. 6

the candles to be racked up into the clamps, and are brought back into position for the next batch without cutting the wicks. The split butt mould also enables more elaborate designs of "self fitting" end to be cast.

Numerous variations in mechanical detail distinguish various machines, but without affecting the essential principles. All these machines work discontinuously; a continuous acting machine, which possesses certain advantages when the water-supply is limited, has been constructed by Fournier & Cie.: it is complicated to work, however, and does not appear to have found favour.

By the use of suitable moulds, candles can be made in various fancy shapes (*cf.* Fig. 7), cabled, spiral, fluted, striped, etc: the candles are ejected from the "spiral" type of mould by imparting a rotary movement to the piston. "Perforated" or "aerated" candles (which are more in favour on the Continent than in England) are made of stearine and moulded with longitudinal perforations up the stem of the candle, which are supposed to afford an internal escape for liquid combustible matter which might otherwise gutter down the outside, and also to allow an up draught of air to assist the combustion. These candles must be made of stearine in order to be sufficiently hard. The popular "Nell Gwynn" candles are moulded with a slightly irregular surface in imitation of the old rolled beeswax candles, and the stems are tapered at the butt-end by pressing the made candles by hand into heated cone-moulds.

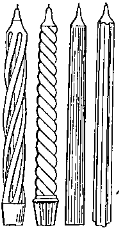


Fig. 7.

Among the various devices which have been proposed to minimise guttering may be mentioned varnishing the outside of the candle with a colour varnish or with cellulose powder in paraffin wax (Powell and Bush, B P. 110579/1916), or moulding the candle with a thin exterior layer of wax harder than that used for the core. The candle material is often coloured with coal tar dyes (*e.g.* Sudan IV, rose Bengal, auramine, brilliant green, induline, methyl violet), and the candles may be decorated with transfers or hand-painting. Ornamental effects are also obtained by cutting grooves in patterns and running in coloured stearine (*cf.* Lodl, Seifens.-Ztg 1936, 63, 263). The "King Alfred's candle," the stem of which is divided by grooves of this kind into sections burning for one hour each, still enjoys favour. By the addition of suitable metallic salts or other substances, candles burning with a coloured flame (Scheuble, G P. 216338), candles (containing esters of amino- or imino- acids with ammonium nitrate) burning with a hot, smokeless flame of low luminosity (Scheuble, G P. 234340), perfumed candles, and medicated candles are obtained.

The production of *night lights* (which were sold originally as mortars or death lights) is still an important business in this country at least. **Night-lights** are short, thick candles with small wicks designed to give a small but constant light over a long period, rather than high luminosity; they were originally made largely

of pressed coconut stearin, and cast direct into paper cases. Now, however, they are chiefly moulded from paraffin wax mixtures in machines *similar to the ordinary candle* mould-ing machine, except that in place of the wick there is a wire which forms a central hole in the night-light; this is then fitted into the case over the wick, which consists of a short piece of taper, stiffened with a coating of hard wax, and fixed in the bottom of the case by means of a small metal sustainer. These night-lights are recommended to be placed in a shallow depth of water during burning, but this precaution is unnecessary for certain uncased types of night-lights which are burnt in glasses. The setting-point of the wax must be carefully adjusted to the climate in which the night-light is to be used, and particular care must be taken during manufacture to avoid the inclusion of dust, as the flame is small and the wick may easily become clogged. The rate of wax consumption is low, being about 40 grains per hour, as against about 120 grains for a candle. A special form of night-light, based on Clark's "pyramid" night-light, which is made in conical shape of neutral fatty material (coconut stearin) and provided with a rush-pith wick, is used for decorative purposes.

The vast majority of candles manufactured in the United Kingdom is employed for domestic purposes: the consumption of candles for religious purposes is also considerable, especially in the Catholic countries, and in Japan and the East. In the industrial field, paraffin wax cables ("bougies") are used as fusible cores for blow-holes in foundry-moulds, and stearine and other candles are employed for lamps and in mines; tallow candles are chiefly made for plumbers' use as a convenient flux (they may serve, incidentally, for illumination), and a considerable quantity is used by certain African tribes for anointing.

Despite the predominance in towns of electrical and gas illumination, the candle industry, though perhaps diminishing in importance, is still in a flourishing condition. Before the War and up to 1931 at least, the average consumption in Great Britain (which, with the inclusion of the Irish Free State, is probably the largest individual consumer) was about 45,000 tons per annum,[1] production being some 10–15% greater, and of an annual value of the order of £2,000,000 in 1924 and £1,570,000 in 1930. The value of the exports of candles, etc., from Great Britain, which amounted to £465,000 in 1913, had fallen to about £335,000 in 1927 and £291,000 in 1929. The total world production of candles (excluding large quantities of candles made by the natives of, for example, China and other tropical countries, from local materials) is certainly over 250,000 tons per annum. France produces about 30,000, Germany about 15,000 (1928), Holland 6,000, and Belgium 4,000 tons of candles per annum. The number of candles may be estimated from the average size, which, in England, is probably about 12 to the lb.

Acknowledgment is made to Messrs. E. Cowles of Hounslow and to Messrs. Price's Patent Candle Co., Battersea, for drawings and for permission to photograph the machinery illustrated above. J. L. and E. L.

[1] Estimates of the paraffin wax candle trade from another source put the figures at 37,000 and 35,000 tons in 1932 and 1933 respectively.

CANELLA ALBA (Fam. Winteranaceæ). White or wild cinnamon, West Indies. The bark, used as an aromatic spice, contains 0·75–1·25% ethereal oil in which *inter al.* eugenol, cineole, caryophyllene have been identified. Formerly the bark was considered to contain "canellin," a substance now recognised to be *d*-mannite. An analysis of the bark gave H_2O, 11·90%; ether extract, 12·73%; proteins, 8·49%; starch, 11·57%; crude fibre, 16·52%; pentosans, 16·72%; mannite, 8·77%; reducing substances (as glucose), 0·76%; ash, 7·4% (Hanus and Bien, Z. Unters. Nahr.-Genussm. 1906, **12**, 395). J. N. G.

CANELLA BARK. The dried bark of *Canella alba* Murr., obtained from Florida and the West Indies in large buff-coloured quills or pieces of about an inch broad. Has a bitter, pungent, acrid taste and odour of a mixture of cloves and cinnamon, due to a volatile oil containing eugenol, cineole, and terpenes. The bark also contains a bitter principle. Used as an aromatic bitter (B.P.C. 1934).

CANFIELDITE *v.* ARGYRODITE.

CANNABINOL *v.* CANNABIS INDICA RESIN.

CANNABIS INDICA RESIN. This substance is the oily resin of Indian hemp, *Cannabis sativa* Linn. (Fam. Cannabinaceæ), also known as Ganjah or Gunjah, from which "hashish" is prepared. The plant itself is indigenous to Central Asia and the Northern and Western Himalayas, and is cultivated mainly in tropical districts of India, Africa, and North America.

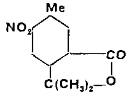
Apart from its use in the form of hashish, or even in the form of the powdered drug, for smoking, it is used to a small extent in medicine. It acts on the central nervous system, producing excitement with hallucinations, with a great feeling of happiness without any fear of terrible surroundings, followed by a deep intoxicated sleep. The after-effects are great depression and lethargy.

The extract of the drug made with various organic solvents contains an oily resinous matter of high boiling-point. It has been investigated by several chemists, but with the exception of the work of Wood, Spivey and Easterfield (J.C.S. 1896, **69**, 539), Bergel and Vögele (Annalen, 1932, **493**, 250), and Cahn (J.C.S. 1931, 630; 1932, 1342; 1933, 1400) the older published results may be regarded as historical.

The principal constituent of the resin is *cannabinol*, the crude, soft brown resin being a mixture of this compound with other substances. The name cannabinol is reserved for the non-crystallisable resin, obtained by the hydrolysis of the pure crystalline acetyl-cannabinol, m.p. 75°, to which Wood and his colleagues assigned the formula $C_{21}H_{25}O_2Ac$, and this has been confirmed by Cahn (*l.c.*).

By nitrating crude cannabinol, trinitrocannabinol melting at 160° was obtained, and by nitrating the higher boiling fractions of the oily residues after separating the acetyl cannabinol, nitro-cannabinolactone, melting at

176°–177°, was obtained. For this compound *Cahn (l c) has established the constitution:*



Cannabinol is phenolic in character.

Bergel and Vogele (*l c*) have effected the synthesis of cannabinolactone, starting from 3 methylphthalic anhydride, and have confirmed the constitution assigned to it by Cahn A further confirmation of the structure of cannabinol is due to Cahn (J C S 1933, 1400), but it does not appear to be the pharmacologically active principle of cannabis resin

E J. P

CANNIZZARITE, $PbS\ 2Bi_2S_3$, as small needles, probably orthorhombic, is of recent formation in the deeper parts of fumaroles with a temperature of 550°–615°, on Vulcano, Lipari Islands Named after Stanislao Cannizzaro (1826–1910) (F Zambonini, O De Fiore, and G. Carobbi, Rend Accad Sci. Fis Mat Napoli, *1925, 31, 28*) L. J S.

CANNIZZARO'S REACTION. The preparation of an alcohol by the action of concentrated aqueous alkali solutions on the corresponding aldehyde, *e g*

$$2C_6H_5\,CHO \xrightarrow{KOH} C_6H_5\,CH_2\,OH + C_6H_5\,CO_2K$$

CANNON SPAR *v.* CALCITE.

CANTHARIDES. *Spanish fly (Lytta vesicatoria).* Dried coleopterous insects used in medicine The specimens chiefly used are *Cantharis vesicatoria* and *Mylabris phalerata* or *cichorii* Preparations of cantharides are employed *externally as rubefacients,* counter-irritants, and vesicants, orally as stimulant diuretics, aphrodisiacs, and emmenagogues. The active principle is *cantharidin*, which is largely replacing cantharides pharmaceutically.

Obtained principally from Spain, other parts of southern and central Europe, and from Russia.

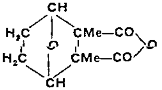
Cantharidin, $C_{10}H_{12}O_4$, stable lactone of cantharidic acid, is obtained by extracting the dried, powdered insects with chloroform, ether or ethyl acetate containing a little mineral acid, evaporating the filtered solution obtained, and finally treating the residue with carbon disulphide or light petroleum to remove fat. The cantharidin may be crystallised from alcohol or acetone to give trimetric plates, m p. 218°, which begin to sublime at 85°. Essentially the same method is used for the determination of cantharidin (Riu, Anal. Fis. Quím. 1931, 29, 164; Iyer and Guha, J. Indian Inst. Sci. 1931, 14, A, 31; Eder and Schneiter, Schweiz. Apoth.-Ztg. 1925, 63, 229, 245). Cantharides contain 0 3–1·1%, the *Mylabris* species somewhat more, about 1–1·5%.

Cantharidin is almost insoluble in water, slightly soluble in alcohol (1 in 1,100 parts by weight) and in ether (1 in 760), more soluble in ethyl acetate (1 in 150), in chloroform (1 in 55), and in acetone (1 in 40), and although *dissolved by glacial acetic acid or concentrated* sulphuric acid it crystallises out unchanged. It is soluble in alkalis to give salts of cantharidic acid.

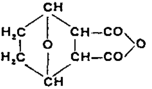
Its detection is possible by microscopical examination of a crystalline sample, especially after sublimation (Denigès, Bull. trav. Soc. Pharm. Bordeaux, 1935, 73, 7). Marchiolo (Boll Chim. farm. 1923, 62, 65) describes its detection in pharmaceutical products and in post mortem examinations, while R. Fischer (Arch Pharm. 1929, 267, 31) details its detection down to a dilution of 1 in 150,000 in 20–30 c c. of urine. A colorimetric method for detection and determination is based on the dense brown colour produced when as little as 0 01 mg. is heated with 1 drop of 10% aqueous formaldehyde and 4–5 c c of sulphuric acid (Denigès, Compt rend 1934, 198, 1783). When cantharidin is nitrated with 50% nitric acid on the water bath, the nitro compound reduced with stannous chloride and the product diazotised and coupled with β naphthol, a violet-red dye is obtained with as little as 0 1 mg (*van* Urk, Pharm. Weekblad, 1929, 66, 313)

It blisters the skin severely, especially when in solution or mixed with fat, R. Fischer (*l c*) gives the minimum dose in lanolin for vesicant action as 0 02–0 015 mg, and Hahn and Taeger (Klin. Woch 1931, 10, 489) have examined this physiological action in detail It should be used with great care, for secondary reactions set in readily. After absorption it produces vaso constriction and during excretion gives rise to irritation of the kidneys and urinary tract. Its pharmacology is discussed by Heubner (Arch exp. Path. Pharm. *1925, 107, 129)* and tolerance to it is treated by Gunn (Physiol Rev. 1923, 3, 41). It has a very strong inhibiting effect on yeast fermentation (Zeller, Biochem Z. 1927, 183, 369, 389).

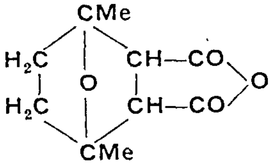
Gadamer suggests the following structure for cantharidin.



(Arch Pharm. 1914, 252, 609; 1917, 255, 277, 315; 1920, 258, 171, *also* Rudolf, *ibid.* 1916, 254, 423). This has not yet received confirmation by synthesis but is supported by the work of Coffey (Rec. trav. chim 1923, 42, 387, 1026), and of Bruchhausen and Bersch (Arch Pharm. 1928, 266, 697), the *latter* having broken down cantharidin to furan and $\alpha\beta$ dimethylsuccinic acid by the action of a dehydrogenating catalyst (palladinised asbestos) at 280°. *Norcantharidin,*



has been synthesised by Bruchhausen and Bersch and also by Diels and Alder (Ber. 1929, 62, B, 554) by the catalytic reduction of the condensation product of furan with maleic *anhydride ; the latter workers also describe a* synthesis of an iso*cantharidin*,



by the same method using 2:5-dimethylfuran.

Many derivatives are described in the work of Gadamer and of Rudolf and a stable hydrazide may be prepared using excess of hydrazine hydrate at 0° (Iyer and Guha, J. Indian Inst. Sci. 1931, **149**, 31). It is claimed that on condensation with ethylenediamine, cantharidin yields a base, $C_{12}H_{18}O_3N_2$, which gives compounds with gold and other heavy metal salts possessing strong bactericidal action (G.P. 269661 ; 272291).

Cantharidin has been detected in the following insects : American " blister beetle " or *Macrobasis albida* by Viehoever and Capen (J. Assoc. Off. Agric. Chem. 1923, **6**, 489), the Javan beetles *Horia debyi*, *Cissites maxillosa*. and *Epicauta ruficeps* (van Zijp, Pharm. Weekblad. 1917, **54**, 295 ; 1922, **59**, 285), and in *Lytta adspersa* (Coll, Rev. farm, 1931, **73**, 17).

CANTON'S PHOSPHORUS *v.* CALCIUM, Calcium Sulphide.

CAOUTCHOUC, RUBBER.

CAPRI BLUE. Oxyazine dyestuff prepared by condensing *p*-nitrosodimethylaniline and dimethyl-*m*-amino-cresol.

CAPRIC ACID, *n*-DECOIC ACID,

$$CH_3{\cdot}[CH_2]_8{\cdot}CO_2H.$$

CAPRINE. *d-a*-Amino-caproic acid (Abderhalden and Weil, Z. physiol. Chem. 1913, **84**, 39).

CAPROIC or HEXOIC ACIDS, $C_5H_{11}{\cdot}COOH$. Seven isomerides are known.

1. *n-Caproic acid*, $CH_3{\cdot}[CH_2]_4{\cdot}COOH$, occurs in the fats ; in cheese ; and, possibly, mixed with certain of its isomerides, in coconut oil ; in St. John's bread ; in the fruit of *Heracleum spondylium* and in the flowers of *Satyrium hircinum* ; and in the fusel-oil from the fermented molasses of mangel-wurzel. Is best prepared by fractionating crude fermentation butyric acid (Lieben and Rossi, Annalen, 1871, **159**. 75 ; 1873, **165**, 118) ; b.p. 204·5° ; sp.gr. 0·9446 at 0°. For synthesis from natural gas hydrocarbons (pentane), *see* Hass and Marshall (Ind. Eng. Chem. 1931, **23**, 352).

2. iso*Butyl acetic acid*, or *γ-methylvaleric acid*,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is present in butter ; may be obtained by the action of hydriodic acid upon hydroxy*iso*caproic acid (Mielck, Annalen, 1876, **180**, 57 ; Fittig and Rühlmann, *ibid.* 1884, **226**, 347), or by the distillation of *iso*butylmalonic acid (König, Monatsh. 1894, **15**, 20 ; Bentley and Perkin, J.C.S. 1898, **73**, 487) ; b.p. 200°–201° ; sp.gr. 0·925 at 0°.

3. *Diethylacetic acid, pseudocaproic acid*, or *a-ethylbutyric acid*, $(C_2H_5)_2CH{\cdot}COOH$, b.p. 190°/756·5 mm. ; d_0^{20} 0·9196, may be obtained by the action of sodium upon ethyl acetate, and treatment of the product with ethyl iodide (Frankland and Duppa, Annalen, 1866, **138**, 221) ; by the hydrolysis of diethylcarbinyl cyanide (Saytzeff, *ibid.* 1878, **193**, 349) ; by reduction of ethyl dichloroethylacetate by sodium amalgam (Markownikow, Ber. 1873, **6**, 1175) ; by heating sodium ethoxide and sodium acetate in a stream of carbon monoxide (Geuther and Frölich, Annalen, 1880, **202**, 308) ; by heating diethylmalonic acid at 170°–180° (Conrad, *ibid.* 1880, **204**, 141) ; by heating *a*-diethyl-*β*-hydroxybutyric acid (Schnapp, *ibid.* 1880, **201**, 70) ; by heating diethylcyanacetic acid with concentrated hydrochloric acid at 160° (Hesse, Amer. Chem. J. 1896, **18**, 749).

4. *Methylpropylacetic acid* or *a-methylvaleric acid*, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CO_2H$, b.p. 193°–194° ; d_0^{18} 0·9279 ; 1 part water dissolves 0·5693 part at 17°, is obtained by the oxidation of the aldehyde, and by the reduction of methylethylacrylic acid (Lieben and Zeisel, Monatsh. 1883, **4**, 37, 63) ; by heating *a*-methyl valerolactone or *iso*saccharin with hydriodic acid and red phosphorus (Liebermann and Scheibler, Ber. 1883, **16**, 1823 ; Kiliani, *ibid.* 1885, **18**, 632) ; by heating *a*-methylpropyl-*β*-hydroxybutyric acid (Jones, Annalen, 1884, **226**, 292) ; it occurs also in rosin oil (Kelbe and Warth, Ber. 1882, **15**, 308).

5. *Methylisopropylacetic acid, isocaproic acid*, or *aβ-dimethylbutyric acid*,

$$(CH_3)_2CH{\cdot}CH(CH_3)CO_2H,$$

b.p. 189°–191°, may be formed from methyl*iso*propylcarbinyl cyanide (Markownikow, Zeitsch. Chem. 1860, 205) ; or by melting camphoric acid with caustic alkali (Crossley and Perkin, J.C.S. 1898, **73**, 16).

6. *Dimethylethylacetic acid* or *aa-dimethylpropionic acid*, $(CH_3)_2C(C_2H_5)CO_2H$, a colourless liquid ; b.p. 187°, m.p. −14°, is formed by the action of hydrochloric acid upon dimethylethylcarbinyl cyanide (Wischnegradsky, Annalen, 1874, **174**, 56), and by the oxidation of the pinacolin of methylethyl ketone (Lawrinowitsch, *ibid.* 1877, **185**, 126).

7. (*a*) *β-Ethylbutyric acid* or *active caproic acid*, $CH_3{\cdot}CH(C_2H_5)CH_2{\cdot}COOH$, b.p. 196°–198°/770 mm. ; d^{15} 0·930, is prepared by the oxidation of the active hexylalcohol obtained from Roman camomile oil (Van Romburgh, Rec. trav. chim. 1886, **5**, 221).

(*b*) *Inactive β-ethylbutyric acid* may be formed by heating secondary butylmalonic acid (Van Romburgh, Rec. trav. chim. 1887, **6**, 153) or from secondary butyliodide, diethylmalonic ester, and sodium ethoxide (Kulisch, Monatsh. 1893, **14**, 561 ; Bentley, J.C.S. 1895, **67**, 267).

CAPROKOL. Hexylresorcinol dissolved in olive oil (Sharp and Dohme, London), B.P.C. 1934. Used as an internal antiseptic.

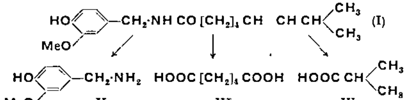
CAPRYL. Syn. for octyl.

CAPSAICIN. Capsaicin is the active principle of various *Capsicum* species (Fam. Solanaceæ) especially *C. annuum* (Spanish

pepper, paprika), and *C. fastigiatum* B. (Cayenne pepper). Capsaicin occurs free in the plants (*cf.* Nestler, Z Nahr.-Genussm 1906, **11**, 661), it may be obtained by direct sublimation from the plant material (Wasicky and Klein, Amer Chem. Abstr 1927, **21**, 1868). *C annuum* contains 0 2%, *C fastigiatum* 0 15–0 5% capsaicin Miko (Z Unters Nahr Genussm 1898, 818) gives details for the extraction of capsaicin from *C annuum* (yield 0 03%), Nelson (Ind Eng Chem 1910, **2**, 419) obtained 0 14% from African cayenne Other interesting extraction methods are described by Tice (Amer J. Pharm. 1933, **105**, 320, 5% yield from capsicum oil) and by Lapworth and Royle (J.C.S. 1919, **115**, 1109)

Capsaicin (I), $C_{18}H_{27}O_3N$, m p 64°–64 5°, crystallises in tablets from light petroleum containing 10% Et_2O (Nelson, J. Amer. Chem Soc 1919, **41**, 1115). It is sparingly soluble in H_2O, soluble in caustic alkalis and is very stable towards hot concentrated alkali hydroxides It is easily soluble in organic solvents except carbon disulphide. It forms a *methyl ether*, m p 77°–78° (from dilute EtOH), and a *benzoyl ester*, silky needles, m p. 74°. It contains one double-bond which adds bromine, and can be hydrogenated (Nelson and Dawson, J Amer Chem Soc 1923, **45**, 2179), the dihydroderivative has m p 65° (from light petroleum)

By oxidation of the methyl ether with permanganate veratric acid was obtained (Lapworth and Royle, *l c*) Acid hydrolysis of capsaicin yielded 4 oxy 3 methoxy benzylamine (vanillylamine) (II), by alkaline hydrolysis under pressure (180°) an unsaturated decenylenic acid, $C_{10}H_{18}O_2$, was obtained. The unsaturated acid may be hydrogenated when an acid, $C_{10}H_{20}O_2$, is obtained which is not *n* caprinic acid (Nelson, *l.c.*). By oxidation of above decenylenic acid Nelson and Dawson (*l c*) obtained adipic (III) and iso butyric (IV) acids respectively. Nelson therefore proposed the following structure for (I):



(I)

II III IV

Nelson and Dawson (*l c*) synthesised the dihydroderivative, m p 65° (*see above*) and finally Späth and Darling (Ber 1930, **63**, [B], 737) synthesised capsaicin

Capsaicin has an extremely pungent taste, 1/800 mg or 1 part in 100,000 parts may still be detected by the tongue, the pungency of the dihydro- derivative is as great as that of capsaicin (Nelson and Dawson, *l c*), that of the methyl ether is very much diminished (Lapworth and Royle, *l c*) For estimation of capsaicin in capsicum fruits, *cf. v.* Fodor (B. 1931, 611), Tice (*l c*) and Wasicky and Klein (*l c*)

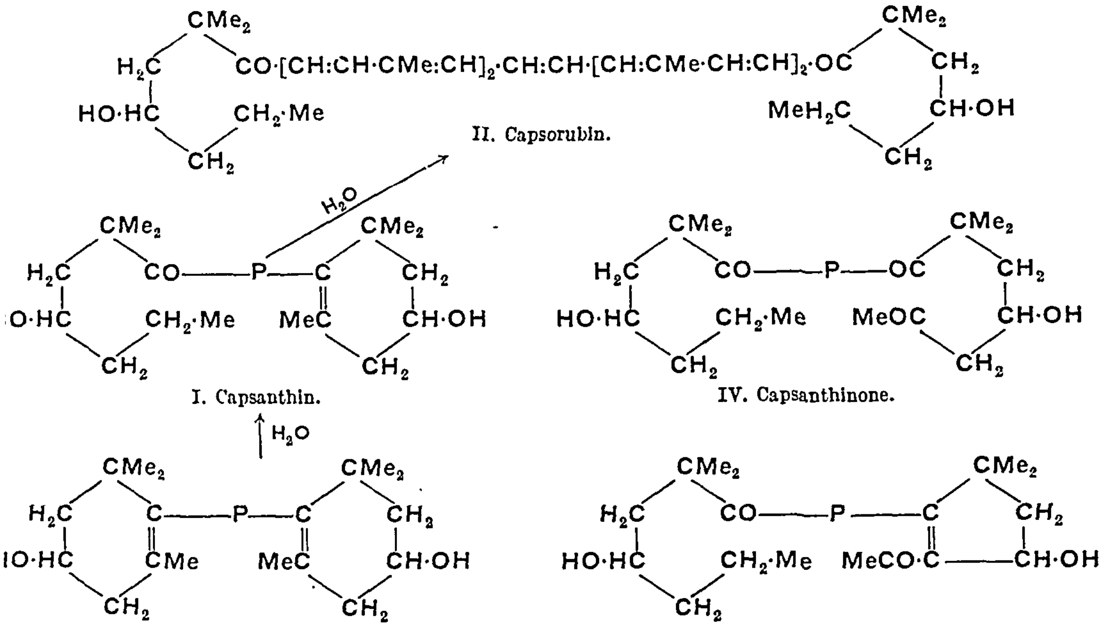
For syntheses of compounds similar to capsaicin, *cf* Nelson (J Amer Chem Soc. 1919, **41**, 2121), Lange, Ebert, and Youse (*ibid* 1929, **51**, 1911), and an interesting paper by Ott and Zimmermann (Annalen, 1921, **425**, 314). Schl.

CAPSANTHIN and CAPSORUBIN. Spanish red pepper or paprika (*Capsicum annuum*) contains a complex mixture of carotenoids which have been examined with considerable success by Zechmeister and *von* Cholnoky (Annalen, 1934, **509**, 269, 1935, **516**, 30) In addition to α- and β carotenes, zeaxanthin, lutein, and kryptoxanthin, two closely related ketonic carotenoids have been isolated by chromatographic methods; the more abundant of these is capsanthin (I), $C_{40}H_{58}O_3$, and the other, present in small amount only, capsorubin (II), $C_{40}H_{60}O_4$. Capsanthin separates in deep carmine-red needles from methyl alcohol, m p. 175°–176°, $[\alpha]_D$ +36° (in chloroform), and exhibits absorption maxima at 543 and 503 mμ in carbon disulphide. It is soluble in alcohol and acetone giving crimson solutions which are deeper in tint than solutions of carotene or lutein of the same concentration. Capsorubin crystallises in violet red needles, m p. 201°, from a variety of solvents and exhibits absorption maxima at 541 5, 503, and 468 mμ in carbon disulphide It may be differentiated from capsanthin by the fact that it is more strongly adsorbed on calcium carbonate.

Catalytic hydrogenation of capsanthin and capsorubin indicates the presence of 10 ethenoid linkages and 1 carbonyl group in the former, and of 9 ethenoid linkages and 2 carbonyl groups in the latter. The remaining two oxygen atoms of both capsanthin and capsorubin are present as easily esterifiable hydroxyl groups. Although capsanthin does not form an oxime, the presence of a carbonyl group has been demonstrated indirectly by the reduction of perhydrocapsanthin with sodium and ethyl alcohol, the number of esterifiable hydroxyl groups then increasing from 2 to 3. The molecular formulæ taken in conjunction with the function of the oxygen atoms and the number of ethenoid linkages clearly establish the monocyclic nature of capsanthin and the aliphatic nature of capsorubin. Since capsanthin does not exhibit vitamin A activity, it cannot contain an unsubstituted β ionone ring, a conclusion which is confirmed by the observation that on oxidation with permanganate capsanthin gives $\alpha\alpha$-dimethylsuccinic acid and dimethylmalonic acid but not $\alpha\alpha$ dimethylglutaric acid (Karrer, Helfenstein, Wehrli, Pieper, and Mori, Helv. Chim. Acta, 1931, **14**, 614). On this evidence satisfactory formulations have been evolved for capsanthin (I) and capsorubin (II); these structures represent the two ketonic carotenoids as two stages in the hydration of zeaxanthin (III)

Oxidation of the diacetate of capsanthin with chromic acid (2 atoms O) gives the diacetate of

capsanthinone (IV), $C_{40}H_{58}O_5$, which, as anticipated, gives anhydrocapsanthinone (V) on treatment with alkali. More drastic oxidation of capsanthin diacetate with chromic anhydride gives capsanthylal (VI), capsylaldehyde (VII), and 4-hydroxy-β-carotenone aldehyde (VIII), the proposed structures being in harmony with their spectrographic properties (Zechmeister and *von* Cholnoky, Annalen, 1936, 523, 101). Reduction of capsanthin with aluminium *iso*propoxide gives capsanthol, m.p. 175°–176°, which exhibits absorption maxima at 508 and 479 mμ in carbon disulphide (Karrer and Hübner, Helv. Chim. Acta, 1936, **19**, 474).



II. Capsorubin.

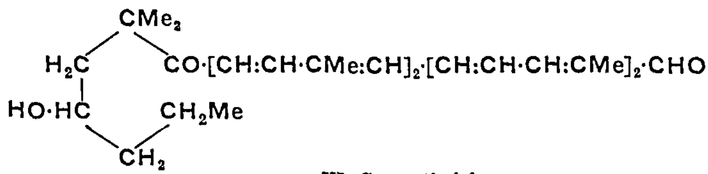
I. Capsanthin.

IV. Capsanthinone.

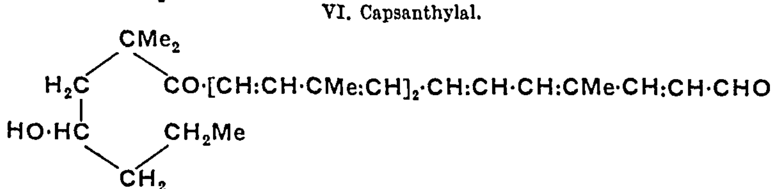
III. Zeaxanthin.

V. Anhydrocapsanthinone.

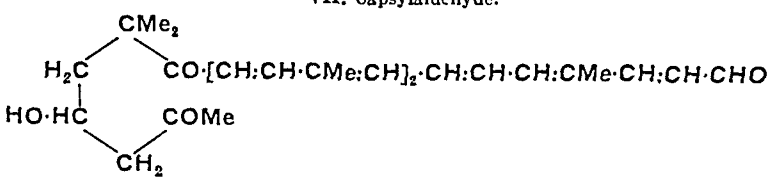
(P=the polyene (C_{18}) chain in Capsorubin.)



VI. Capsanthylal.



VII. Capsylaldehyde.



VIII. 4-Hydroxy-β-carotenone aldehyde.

I. M. H., R. F. P., and F. S. S.

CAPSICUM. Much confusion still exists with regard to the various species of red peppers, which include capsicums or chillies, Cayenne pepper, paprikas, and pimentos. According to the British Pharmacopœia, capsicums are the dried ripe fruits of *Capsicum minimum* Roxb., (Fam. Solanaceæ), whilst the United States Pharmacopœia defines them as the dried ripe fruit of *Capsicum frutescens* Linn. (Fam. Solanaceæ). Red peppers appear to have come originally from the American tropics and are first mentioned in a letter by Peter Mertyn,

dated September, 1493. Within a very few years they were brought to Europe, and their cultivation has now spread to numerous parts, including Sierra Leone, Nyasaland, Zanzibar, Bombay, Natal, Hungary, and Spain, whilst another variety is grown in Japan. Irish cultivated every known variety for 4 years in the Missouri Botanical Garden, and came to the conclusion that there are only two species of the genus, one an annual or a biennial herbaceous plant, the other a perennial shrub. The first is the one most commonly cultivated in Europe and gives rise to the paprikas of Hungary and the pimentos of Spain, though these latter are frequently called Spanish paprika or simply paprika. These fruits are derived from *Capsicum annuum*. The second type is the species *Capsicum frutescens*, the fruits of which never ripen properly in temperate climates. This type gives rise to two varieties: one known as *Capsicum frutescens* proper and the other as *Capsicum frutescens baccatum* or simply *Capsicum baccatum* Linn. *Capsicum minimum* is a member of the *frutescens* variety. It is held by some that the Japanese capsicum is a hybrid between *Capsicum annuum* and *Capsicum frutescens*. The capsicum plant belongs to the same family as the potato and the tomato, and it may generally be said that whilst cultivation improves the size and colour of the fruit, the flavour and aroma are diminished.

African chillies measure from 1 to 2 cm. in length, and are about 3–7 mm. in breadth. Japanese chillies measure 3–4 cm., while Bombay and Natal capsicums may be as much as 10 cm. or more. The small varieties are used chiefly in England and America, but the larger ones are preferred on the Continent. African chillies are a dull orange-red in colour, the Japanese are a bright red, whilst Hungarian and Spanish paprikas are a very bright red and are used almost as much for their colouring properties as for their flavour.

Microscopic Appearance.—Wallis (Pharm. J. 1901, [iv], 13, 552; 1902, [iv], 15, 3) has studied the microscopic characteristics of the capsicums exhaustively, and summarises his results as follows:

C. minimum.	*C. annuum.*	Japanese chillies.
Thick and straight-walled rectangular cells with few pits, often arranged in groups of 5 to 7 in a row and with a uniformly striated cuticle. Size of cells 25μ to 60μ in either direction.	Irregular polygonal cells with evenly thickened walls, traversed by numerous well marked, simple pits. The cuticle shows striated ridges. Size of cells 50μ to 100μ long, and 25μ to 50μ wide.	Cells with strongly thickened walls and a radiated lumen. The pits only rarely penetrate the whole thickness of the wall. No visible striation. Size of cells 30μ to 80μ long and 15μ to 45μ wide.
Delicate thin-walled cellulose cells.	Several layers of cuticularised collenchymatous cells, having a rounded outline and very few pits.	A single layer of regular polygonal cells with cuticularised fairly thick walls, traversed by numerous pits, which give them a beaded appearance.

Chemical Composition.—H. E. Cox ("Chemical Analysis of Foods," 1926, 157) gives the following as the average analytical figures for cayenne pepper and paprika:

	Cayenne.	Paprika.
Moisture	7·5–10·0	7·0–7·6
Ash	5·1–6·4	6·1–6·5
Water-soluble ash . .	2·6–3·5	4·7–5·0
Ether extract . . .	15·5–19·2	9·5–11·4
Alcohol (60%) extract .	24·0–30·0	14·7–15·8
Crude fibre	17·5–24·5	14·5–15·0
Nitrogen	1·8–2·2	2·4–2·9
Starch	0·5–1·5	—

Numerous other figures have been published, notably by Winton, Ogden, and Mitchell (Ann. Rep. Connecticut Exper. Station, 1898, 200), Doolittle and Ogden (J. Amer. Chem. Soc. 1908, 30, 1481), and Tolman and Mitchell (Ind. Eng. Chem. 1913, 5, 747).

Béla von Bittó (Landw. Versuchs Stat. 1895, 46, 309) mentions that 0·7% of free fatty acids, chiefly palmitic, are present in the seeds, and these acids are responsible for precipitation in tinctures made from the ground fruits.

Nelson (J. Amer. Chem. Soc. 1919, 41, 1115; 1920, 42, 597; 1923, 45, 2179) has synthesised capsaicin, $C_{18}H_{27}O_3N$, the pungent principle of cayenne peppers, by condensing vanillylamine and a decenoic acid. Fruits of Sierra Leone and Japanese chillies and *Capsicum annuum* do not contain capsaicin (*see, however,* Miko, Z. Unters. Nahr. Genussm. 1898, 818). Hungarian paprikas contain up to 0·01% of capsaicin, but it is not present in Spanish paprikas.

Vitamin C.—J. L. Svirbely and A. Szent-Gyorgyi (Biochem. J. 1933, 27, 279) have shown that paprika pepper is one of the richest sources of Vitamin C, of which it contains about 0·2%.

Colouring Matter, see CAPSANTHIN AND CAPSORUBIN.

Assay.—K. von Fodor (Z. Unters. Lebensm. 1931, 61, 94) has shown that $\frac{1}{50}$ mg. capsaicin in dry ether solution gives an intense blue coloration with vanadium oxychloride. A similar reaction, which is, however, not so sensitive, may be obtained by treating a clear extract (5 c.c. ≡ 1 g. of sample) in dry acetone with 9 drops of concentrated hydrochloric acid and 0·1 g. of ammonium vanadate. The colour varies from blue (for 0·08%) through green to green-brown (for 0·01% of capsaicin). The brown colour is due to the presence of carotene. The blue compound has the composition $C_{18}H_{26}O_3N{\cdot}VOCl_2$.

L. F. Tice (Amer. J. Pharm. 1933, 105, 320) describes a method of determining the capsaicin in paprika by extracting 2 parts by weight of the dried fruit for 30–60 minutes with 100 vols. of dry acetone; 5 c.c. of the extract are treated with 1 drop of vanadium oxychloride solution and the colour obtained compared with that given by solutions of pure capsaicin in acetone coloured by previous extraction of capsaicin-free paprika.

The sharp taste of cayenne pepper is due to the stimulation of the nerves in the mouth and throat, and it has been suggested (J. C. Munch, J. Assoc. Off. Agric. Chem. 1930, 13,

383) that the best method of determining the pungency of cayenne peppers is by taste. A solution of capsaicin is very satisfactory, but difficult to prepare, and piperine is employed as a substitute. A standard is prepared by dissolving 16 mg. of piperine in 1 litre of 10% sucrose solution, and the amount of capsicum required to produce the same effect in the throat is estimated.

W. Pfahl and A. Rotsch (Z. Unters. Lebensm. 1933, 65, 452) have demonstrated that the presence of paprika in sausages may be proved by means of a characteristic colour reaction. The fat is extracted and saponified, the fatty acids being converted into their calcium salts, which are washed and dried and extracted with 96% alcohol. After evaporation of the alcohol the residue is treated with concentrated sulphuric acid, and in the presence of paprika a purple colour is obtained.

Preservative Action.—J. W. Corran and S. H. Edgar (J.S.C.I. 1933, 52, T, 149) have shown that cayenne pepper and its oleoresin exert no inhibitory action towards fermentation by yeast.

Adulteration. — Powdered cayenne pepper may contain olive oil, which is added by the grinders in order to facilitate the process. In the eastern part of Europe, where paprika is used considerably as a condiment, adulteration is rife, the addition of maize meal, sawdust, bran, and extracted sunflower seeds, together with a dye, being common, while in 1923 more than a thousand people were partially poisoned owing to the addition of 20% of red lead.

Standards.—The monograph in the British Pharmacopœia, 1932, is almost identical with that of 1914, but it is specified that the pungency of capsicum is unaffected by alkalis, although it is destroyed by potassium permanganate. The ash must not exceed 7·0%. The regulations under the "Canadian Food and Drugs Act," 1928, describe cayenne pepper as being the dried ripe fruit of *C. frutescens*, *C. baccatum*, or other small-fruited species of capsicum. It must contain not less than 15% of non-volatile ether extract and not more than 1·5% of starch, 28% of crude fibre, 8% of total ash, or 1·25% of ash insoluble in hydrochloric acid. T. McL.

CAPSICUM RESIN. The commercial article known as capsicine is an oleo-resinous body of indefinite composition. The fruits of *Capsicum minimum*, known commonly as chillies, are used to impart a hot taste to pickles and similar substances, and in powder form are known as cayenne pepper. It is used to some extent in medicine and is to be found in cheap brands of ginger beer, being used to give "hotness" at less expense than if ginger were used. If the crushed fruits are exhausted with ether, the resulting extract will contain a considerable amount of fatty oil. The ethereal extract is itself extracted with alcohol, and this alcoholic extract nearly free from fatty oil forms the capsicine of commerce. The substance chiefly responsible for the hot and acrid taste of capsicum is a body discovered by Thresh (Pharm. J. iii. 6, 941) and to which he gave the name capsaicin (*q.v.*). E. J. P.

CAPSORUBIN *v.* CAPSANTHIN.

CAPSULARIGENIN *v.* CAPSULARIN.

CAPSULARIN, $C_{22}H_{36}O_8$, m.p. 175°, $[\alpha]_D$ −23·6°, was isolated by Saha and Chowdhury (J.C.S. 1922, 121, 1044) from jute leaves, *Corchorus capsularis*, in 0·6% yield on the weight of the dry leaves. The glucose obtained on hydrolysis with sulphuric acid is, according to the authors, in optically inactive admixture, although this is questionable. The aglucone is termed *capsularigenin*. E. F. A.

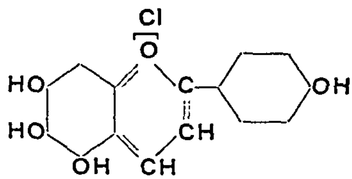
CAPUT MORTUUM. A residue from destructive distillation, *e.g.* ferric oxide.

CARAJURA or **CRAJURA** *v.* CHICA RED OR CARAJURA.

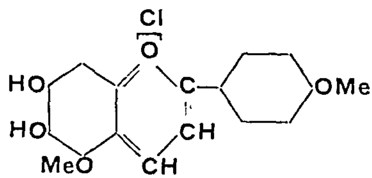
CARAJURETIN *v.* CARAJURIN.

CARAJURIN is the main anthocyanin colouring matter of the rare red pigment carajura, prepared by the South American Indians from the leaves of *Bignonia chica*. It was isolated and analysed by Chapman, Perkin, and Robinson (J.C.S. 1927, 3015), and given the empirical formula $C_{17}H_{14}O_5$. Carajurin crystallised from benzene in garnet-like prismatic needles, and was found to have phenolic properties and to combine easily with acids to form well-defined crystalline oxonium salts. It contains two methoxy groups, and on demethylation with boiling hydriodic acid and treatment with cold pyridine it yields *carajuretin*. Since there is no tendency to pseudo-base formation, a hydroxyl at 3 is improbable.

The suggested formula (I) for carajuretin hydrochloride was confirmed by the synthesis of scutellareinidin chloride, an anthocyanidin related to the flavone scutellarein, which resembled carajuretin hydrochloride in every respect. Carajurin hydrochloride is probably (II).



I.



II.

Carajura also contains *carajurone*,

$C_{15}H_9O_5{\cdot}OMe$,

insoluble in benzene, which is probably carajuretin monomethyl ether.

The resemblance in type between carajurin and one of the less common flavones is of interest, since the natural anthocyanins are much less varied in type than the anthoxanthins. R. S.-M.

CARAMBOLA. The fruit of *Averrhoa Carambola* Linn., a tropical tree grown in America, China, India and Hawaii. It resembles a cucumber in general form, attaining a length of

4–5 in, and having deeply ribbed sides shows a cross-section of the form of a five pointed star. It is highly acid and largely used for the making of mixed pickles, but is sometimes eaten raw when fully ripe. A similar but somewhat smaller species (*A. Bilimbi* Linn) known generally as "bilimbi" (or in the Philippines as "camias") finds similar uses. The fruits weigh from ½ to 1½ oz.

According to Del Rosario (Philippine J. Sci. 1913, 8, 59) a considerable proportion of the acidity of both fruits is due to oxalic acid, although other writers express some doubt on this matter.

Recorded analyses (expressed as percentage of green fruit) are ·

	Solids.	Protein.	Fat	Acids.	Reducing sugars	Fibre	Ash.
Carambola[1]	6 09	0 24	0 74	—	—	0 61	0 42
Carambola[2]	8 22	0 72	0 76	1 01[4]	3 40	1 24	0 42
Bilimbi[3]	5 14	0 68	1 39	—	—	0 61	0 36

[1] Philippine fruit Adriano *et al* (Philippine Agric 1925, 14, 57)
[2] Hawaiian fruit quoted by Winton, "Structure and Composition of Foods" Wiley, New York, 1932–1935
[3] Philippine fruit Adriano *et al.* (Philippine Agric 1929, 18, 119)
[4] Calculated as oxalic acid

A. G. Po.

CARAMEL is the brown substance produced by the action of heat on glucose or invert sugar, and used for colouring or flavouring various drinks and foods All shades of brown, to nearly black, can be obtained according to the method of manufacture, which varies with the use for which the product is intended. Originally, the sugar was heated to frothing point in an open pan; later, an alkali hydroxide or carbonate was added It is now usual to conduct the operation in a closed vessel, with the addition of ammonia or ammonium salts (Salamon and Goldie, J.S C.I. 1900, 19, 301; Ling and Nanji, *ibid.* 1922, 41, 151T) or of calcium carbonate (*Garino-Canina, Notiz. chim. ind. 1927*, 2, 133). The product may be purified by steam distillation (Albrecht, B P. 346136) or dialysis (Beal and Zoller, J. Amer. Pharm. Assoc. 1914, 3, 495). The manufacture of caramel from molasses is described by Akkermann (Arch. Suikerind. Ned.-Indië, 1930, 38, 677). Baja (Requind. 1932, 1, 52, 74; 1932, B, 1100) has investigated the effect on the product of glucose, dextrins, and proteins in the starting material; he recommends replacing part of the glucose by invert sugar or honey, but not by molasses. According to Ripp (Z. Ver. deut. Zucker-Ind. 1926, 627) the nitrogenous substances present determine the depth of colour of the product.

Caramel forms a porous, amorphous, brittle mass of m.p. 134°–136°, deliquescent and partially soluble in alcohol. It has a more or less bitter taste and is not fermentable. Its spectrum has no definite absorption bands, but the blue side is extinguished, as in the case of ferric chloride (Blyth and Cox, "Foods," 1927, 7th ed., p. 93). The product of Garino-Canina's method of manufacture contains a negative colloid which is flocculated by hydrochloric acid at p_H 2 05 (Clayton, "Colloid Aspects of Food Chemistry and Technology," 1932, p. 315); the adsorption of the colloid on charcoal has been investigated by Hauge and Willaman (Ind. Eng. Chem. 1927, 19, 944) Similarities with the colloids of molasses have been pointed out by Joszt and Molinski (Kolloid Beih. 1935, 42, 367)

Caramel is a complex mixture, and not much is known of its constitution. Its colloid character is discussed by G. von Elbe (J. Amer. Chem Soc. 1936, 58, 600). Its principal constituents appear to be *caramelan*, *caramelen*, and *caramelin*; Marcusson (Z. angew. Chem. 1927, 40, 1233) found also caramelic acid, but the existence *of this is denied by Fuchs (ibid. 1928, 41, 85).*

Caramelan, $C_{12}H_{18}O_9$ or $C_{24}H_{36}O_{18}$, the main constituent of caramel, is obtained nearly pure by heating a lævulose solution on a water bath or by heating sucrose at 170°–180° till 12% of its weight is lost. It is a brittle brown solid, bitter and odourless, m.p. 136°, deliquescent, soluble in 84% alcohol, pyridine, methyl alcohol, or hot glacial acetic acid, insoluble in ether and benzene. It reduces Fehling's solution, silver nitrate and gold salts. Alcoholic lead acetate precipitates $C_{12}H_{16}O_8{\cdot}PbO$, ammoniacal lead acetate, $C_{12}H_{16}O_8{\cdot}2PbO$; resorcinol or phloroglucinol gives a red precipitate soluble in alcohol or alkalis. Caramelan forms a yellow *tetra acetate*, m.p 107°, insoluble in water or ether, soluble in benzene, hot alcohol, or glacial acetic acid, a pale buff coloured *tetrabenzoate*, m p. 105°–108°, soluble in acetone, chloroform, alcohol, or benzene, insoluble in water, ether and light petroleum, and a yellow *tetranitrate* which inflames violently on warming and is readily soluble in alcohol, ether or benzene, insoluble in water. It appears to be a tetrahydroxy alcohol and to contain one CO or CHO-group per C_{24} unit. *See* Cunningham and Dorée (J.C.S. 1917, 111, 589).

Caramelen, $C_{36}H_{48}O_{24}$, is separated from caramelan by extracting with 84% alcohol, exhausting with cold water, and precipitating with absolute alcohol (Blyth and Cox, *l.c.*). It is a brittle solid, darker than caramelan and of great tinctorial power, readily soluble in water but not deliquescent, sparingly soluble in alcohol, insoluble in ether. It reduces Fehling's solution and forms compounds with lead similar to those of caramelan (Cunningham and Dorée, *l.c.*).

Caramelin, $C_{24}H_{26}O_{13}$ or $C_{96}H_{102}O_{51}$, is a nearly black, infusible substance, a mixture of isomerides *A*, *B*, and *C*. *A* is soluble in cold water, *B* soluble in hot water, and *C* insoluble. *A* passes into *B* on evaporating its aqueous solution. The soluble forms reduce Fehling's solution and silver and gold salts, and give precipitates with lead salts (Cunningham and Dorée, *l.c.*).

Detection and Estimation of Caramel.—Some *wines contain natural caramel* (Mastbaum, Z. Unters. Lebensm. 1933, 66, 254), but in general artificial addition is to be suspected if the brown colour of a liquid does not disappear on shaking with tannic acid (Blyth and Cox,

op. cit.). Fullers' earth also removes the colour due to caramel. Paraldehyde and alcohol give a brown precipitate soluble in water ; the colour of this solution may be used as a measure of the caramel present (Blyth and Cox ; Woodman, "Food Analysis," 1924, 2nd ed., p. 83 ; Heuss, Z. ges. Brauw. 1918, **41**, 108). Caramel may also be estimated colorimetrically after extraction by a mixture of amyl alcohol, toluene and tartaric acid (Williams, U.S.P. 1689901) or spectroscopically by absorption of the blue end of the spectrum by an aqueous solution (Stolle, Chem. Zentr. 1899, (5), **3**, ii, 1099). From the solution of the paraldehyde precipitate, phenyl hydrazine precipitates a substance similar to an osazone but amorphous ; this can be used for the estimation of caramel. Lead acetate gives a yellow to brown colour if caramel is present. The presence of hydroxymethylfurfural associated with caramel is shown by a red colour with resorcinol (Ronnel, Ann. Falsif. 1912, **5**, 517), a violet colour with β-naphthol in sulphuric acid, or an orange-yellow colour with phenol in sulphuric acid (Schenk, Apoth.-Ztg. 1914, **29**, 202 ; J.S.C.I. 1914, **33**, 369). Reduction of Fehling's solution may be used for the estimation of caramel if any dextrose present is previously removed. Methods of determining caramel on coffee beans roasted with sugar have been investigated by Fresenius and Grünhut (Z. anal. Chem. 1897, **36**, 225) ; Hilger's method, modified by Rifé and Medrano (Anal. Fís. Quím. [tecn.], 1929, **27**, 313), is said to be the best. It consists in extracting with water and 90% alcohol (1:1), evaporating and weighing the residue, subtracting a constant to allow for soluble constituents of the coffee itself. In milk, caramel is detected by a bluish-violet colour produced on covering the curd with concentrated hydrochloric acid (Blyth and Cox, *op. cit.*).

Caramel may itself be adulterated with coal-tar dyes. These are detected by double dyeing from a very dilute solution, using tartaric acid as a fixing agent (Noël, Pharm. Zentr. 1926, **67**, 33). The detection of sugar, starch syrup, and invert sugar may be carried out by a modification of Kruisheer's method (Aleksandrov and Salischtscheva, Schr. zentr. Forschungsinst. Lebensm. U.S.S.R. 1933, **4**, 33).

CARANA. A soft oleo-resin allied to Brazilian elemi, probably derived from *Protium carana* March. and allied species.

CARAPA OIL. *Crabwood oil, Touloucouna oil, Andiroba oil.* These names comprise a group of similar oils from the seeds of species of *Carapa* (Fam. Meliaceæ). The most important of these oils, known as *crabwood oil*, or, in Brazil, as *Andiroba oil*, is obtained from *Carapa guianensis* Aubl. (=*C. guyanensis* Aubl.), a tree growing in the West Indies and in Central and South America. The oil is produced by crude native methods and is used locally as a liniment and insect-repellent (*cf.* de Verteuil, Agric. Rec. Trinidad, 1899, August, p. 17), and also as an illuminant. Its industrial use for soap-making is being developed (166,000 litres of oil were exported from Brazil in 1920). The characteristics of the oil are as follows : m.p. 28°C. (partly liquid at 15°C.) ; d_{15}^{100} 0·8572 ; acid value, up to 37 ; saponification value 197 ; iodine value 57·3–64·5 ; unsaponifiable matter 0·6% ; f.p. of the fatty acids 35·8°C. (*cf.* Bolton and Hewer, Analyst, 1917, **42**, 35 ; Bull. Imp. Inst. 1928, **26**, 411). Several samples of oil examined by Bolton and Hewer were found to display slight optical activity.

A similar oil is obtained from the African tree *C. procera* DC. (=*C. guyanensis* Oliv., *C. touloucouna* Guill. and Perr., *C. guineensis* Don. and Sweet., *C. microcarpa* A. Chev.): Lewkowitsch (Analyst, 1909, **34**, 10) gives the following figures for the cold-pressed oil from seeds from Sierra Leone : d_{15}^{15} 0·9272 ; m.p. 15°–36°C. ; saponification value 197·1 ; iodine value 75·7 (Wright, Bull. Dept. Agric. Trinidad, 1910, (9), No. 65, gives iodine values of 58·5–67·7—for *C. procera* ?) ; mean molecular weight of the fatty acids 291·5. Lewkowitsch also reports data for a hot-pressed oil.

C. grandiflora, Sprague, from Uganda (Lewkowitsch, Analyst, 1908, **33**, 184) is a distinct species, but yields a similar oil. J. L. and E. L.

CARAWAY. The dried fruit (seed) of *Carum Carvi* Linn. (Fam. Umbelliferæ), a native of West Africa, and largely cultivated in Europe and America. The plant is a biennial, growing to a height of 2–3 ft., and is not unlike parsley in appearance. It flowers in May and June, but the best fruits are only collected in the second year. The mericarps are usually separate from the pedicel, and vary from 3 to 7 mm. in length and 1·5 to 2 mm. in breadth ; they are slightly curved and taper towards each end. The cross-section of the fruit is almost that of a regular pentagon, the commissural surface being slightly greater than the four comprising the dorsal surface. The cross-section also shows the presence of six vittæ or oil cells, of which two are on the commissural side. The fruit is similar to fennel seed, but is shorter and more slender. It is largely used for flavouring purposes, though it is not as popular as formerly. It is also used as a carminative.

Microscopic Appearance.—The epidermal cells have a very thick striated cuticle, and stomata are present. The mesocarp consists of more or less collapsed parenchyma, though the reticulated cells found in fennel are absent. The vittæ are very large, and may be as much as 350μ in tangential diameter. The endosperm and embryo are very similar to fennel in structure, being without grooves and containing fixed oil, aleurone grains (*q.v.*), and rosette aggregates of calcium oxalate about 1μ in diameter.

Chemical Composition.—H. E. Cox, "Chemical Analysis of Foods," 1926, p. 171, gives the following composition :

	%
Moisture	11·5–15·5
Ash	5·5– 6·7
Water-soluble ash	2·0– 2·2
Volatile oil	2·7– 8·2
Fixed oil and resin	6·2–10·1
Crude fibre	17·5–22·3
Nitrogen	5·9– 6·4

Probably the most satisfactory method of determining the amount of essential oil present in the seeds is by the process of Cocking and Middleton (Quart. J. Pharm. 1935, **8**, 435).

The crushed seeds are mixed with brine solution, distilled, and the vapours passed through the top of a condenser into a graduated tube, in which the oil is collected, whilst the condensed water is returned to the distillation flask. These authors find that the yield of oil is increased by about 0·6–0·7% if the fruits are powdered before distillation, but that the powdered seeds tend to lose volatile oil on keeping. Commercial powdered seeds contain from 2·3 to 3·9% of volatile oil. For further details of the oil, *see* CARAWAY, ESSENTIAL OIL OF.

Standards.—The British Pharmacopœia requires an ash content of not more than 9% with acid-insoluble ash less than 1·5%. The United States Pharmacopœia requires an ash content of not more than 8%.

Adulteration.—Caraway seeds are often adulterated with exhausted (extracted) fruits, these are much darker in colour than those which have not been treated. T. McL.

CARAWAY, ESSENTIAL OIL OF. The oil distilled is from the fresh caraway seed (*v. supra*). The yield of oil is 4·0–6·5%.

Constituents.—The chief constituent of this oil is carvone (*q.v.*), to which the odour and taste are mainly due. A good oil contains at least 50% of carvone. The remainder of the oil consists of the terpene *d*-carvene, identical with *d*-limonene, and in addition small quantities of dehydrocarvone, carveole, dehydrocarveole. Carvone forms a characteristic crystalline compound with sulphuretted hydrogen when the latter is passed into a solution of the oil in alcohol saturated with ammonia gas.

Characters.—It is a colourless or pale yellow oil, sp.gr. 0·910–0·920 at 15·5°, optical rotation +70° to +80°, n_D^{20} 1·485–1·492. It is soluble in an equal volume of alcohol 90%, and in 7 vols. of alcohol 80%. The percentage of carvone is determined by the hydroxylamine method. Caraway oil is used chiefly for flavouring purposes and in medicine as a carminative. C. T. B.

CARBAMIC ACID, $H_2N·COOH$. *Aminoformic acid.* An acid not known in the free state. *Ammonium carbamate* is, however, met with in freshly sublimed commercial ammonium carbonate, and may be prepared by mixing gaseous ammonia and carbon dioxide. Obtained also by the action of alkaline solution of potassium permanganate on albumen, leucine, tyrosine, and glycocoll.

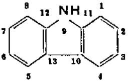
CARBASONE, *p*-carbaminophenylarsonic acid (*v.* ARSENICALS, ORGANIC).

CARBAZIDE *v.* CARBAZOIMIDE.

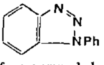
CARBAZINES and CARBAZONES *v.* ACRIDINE DYESTUFFS.

CARBAZOIMIDE, *carbonyl azide* (has been called *carbazide* and *carbonyl nitride*), $N_3·CO·N_3$. Long needles with a penetrating odour, obtained by extracting with ether a cold mixture of solutions of 2 mols. sodium nitrite and 1 mol. carbohydrazide hydrochloride. Explodes violently on friction and even when exposed to light. Very soluble in water, alcohol, and ether. Extremely volatile. The aqueous solution decomposes slowly into carbon dioxide and hydrazoic acid (Curtius and Heidenreich, Ber. 1894, 27, 2684; J. pr. Chem 1895, [ii], 52, 454).

CARBAZOLE, $C_{12}H_9N$,



Syntheses.—Carbazole is formed by pyrolysis of aniline, diphenylamine (Graebe, Ber. 1872, 5, 377; Annalen, 1873, 167, 128), methyl diphenylamine (*idem. Annalen, 1874, 174, 181*), or 2-aminodiphenyl (Blank, Ber. 1891, 24, 306). It is produced in good yield by heating 2:2′-diaminodiphenyl with 25% H_2SO_4 or 15% HCl at 200°C. (Tauber, Ber. 1891, 24, 200), or by reduction of the diazonium solution prepared from 2:2′-diaminodiphenyl, *e.g.* with potassium hydrosulphide (*idem*, *ibid.* 1893, 26, 1703). 1-Phenyl-benztriazole,



itself obtained from *o*-aminodiphenylamine and nitrous acid, yields carbazole when heated at 360° (Graebe and Ullmann, Annalen, 1896, 291, 16).

Tetrahydrocarbazole, obtained on boiling cyclohexanone phenylhydrazone with hydrochloric acid (W. Borsche *et al.*, Annalen, 1908, 359, 49) when mixed with hydrogen and passed *over a catalyst containing copper, chromium,* and barium oxides, and Florida earth is converted to pure carbazole (F.P. 744595, 1933). Other dehydrogenating agents may be used.

Carbazole is formed in the dry distillation of strychnine and in the distillation of brucine with zinc dust (Loebisch and Schopp, Monatsh. 1886, 7, 614).

Manufacture from Coal Tar.—Carbazole is produced in the dry distillation of coal (for discussion, *see* Stemart and Schulz, Chim. et Ind. 1934, 31, 507–513, 766–772), and appears in the anthracene fraction of coal tar boiling between 320° and 360°C. The solids deposited on cooling this fraction contain about 30% of anthracene, 22% of carbazole, and 48% of phenanthrene and other hydrocarbons (F. M. Clark, Ind. Eng. Chem. 1919, 11, 204). It may be isolated from the raw anthracene by conversion to its potassium derivative with solid KOH and subsequent decomposition of the derivative with water.

$$C_{12}H_8·NH + KOH = C_{12}H_8·NK + H_2O$$

A separation of a mixture of anthracene hydrocarbons and carbazole is effected either by extraction of the former with carbon tetrachloride (U.S.P. 1672630) or of the latter with crude pyridine bases (E. Kenngott, Chem.-Ztg. 1932, 56, 969). Hydrogenation at high temperatures and pressures of tar fractions with a molybdenum - chromium - manganese catalyst (B.P. 340585) or with a catalyst composed of alkali or alkaline earth metals or their hydrides (F.P. 733704) yields a product from which carbazole may be isolated by vacuum distillation and crystallisation from the crude condensate

Pure carbazole may be obtained from impure commercial samples by extraction of accompanying phenanthrene with solvent naphthas, sulphonation of the anthracene with cold 98% sulphuric acid, and sublimation of the residual carbazole (Clark, Ind. Eng. Chem. 1919, **11**, 208).

Properties.—Carbazole may be obtained as leaves and needles by sublimation or by recrystallisation from toluene. It has m.p. 245°, b.p. 354°–355°, and is weakly triboluminescent.

Chemical Character and Tests.—Carbazole is an extremely stable compound and is unchanged by distillation over glowing zinc dust (Graebe, 1872, B, 5, 13). It is only very weakly basic and dissolves unchanged in cold conc. H_2SO_4, and is reprecipitated on dilution with water.

Carbazole may be reduced catalytically partially or completely. On its reduction with red phosphorus and hydriodic acid " carbazolene," or 1:2:3:4:10:11-hexahydrocarbazole, is produced (Graebe and Glaser, Annalen, 1872, **163**, 352). Reduction of carbazole with sodium and amyl alcohol yields 1:4-dihydro- and 1:2:3:4-tetrahydro-carbazole (Zanetti, Ber. 1893, **26**, 2006).

The only well characterised products which have been obtained by oxidation of carbazole are two isomeric dicarbazyls, m.p. 220° and 265° respectively (Perkin and Tucker, J.C.S. 1921, **119**, 216). The former is 9:9'-dicarbazyl (McLintock and Tucker, *ibid.*, 1927, 1214).

Carbazole gives several colour reactions, *e.g.* it may be detected in the presence of diphenylamine by dissolving the mixture in benzene, carefully adding a few drops of 70% H_2SO_4, avoiding mixing, and finally adding 1 drop of 3% H_2O_2. In the presence of carbazole a green tint appears at the interface of the two layers (Stemart and Schulz (*l.c.*)).

On melting together carbazole and oxalic acid " carbazole blue," the formate of tri-(3)-carbazyl carbinol, $[C_{12}H_8N]_3C(OH)$, is produced (Bamberger and Müller, Ber. 1887, **20**, 1903 ; Copisarow, Trans. Ceram. Soc. 1920, 1542).

Derivatives of Carbazole.—Derivatives of carbazole may be obtained by total syntheses similar to those already mentioned for the parent compound or, usually more conveniently, starting from carbazole itself.

They may be considered in the two classes :

(1) N-derivatives.
(2) C-derivatives.

(1) N-*derivatives.*—Carbazole reacts with solid caustic potash giving a N-potassium derivative, and with methyl magnesium iodide giving the compound, $C_{12}H_8N{\cdot}MgI$.

N-alphyl-carbazoles may be prepared from the potassium compound and alphyl-halides, preferably iodides, under fairly mild conditions.

N-acyl-carbazoles may be obtained from the potassium or magnesium derivative and acyl halides.

N-*acetylcarbazole*, m.p. 76°, is formed from carbazole and acetic anhydride in the presence of sulphuric acid or ferric chloride at 98°C. (Böeseken, Rec. trav. chim. 1912, **31**, 361). N-*oxymethyl carbazole*, m.p. 127°, is formed from formaldehyde, carbazole, and alkali carbonate in alcohol (G.P. 256757). On heating with acids it is converted to 3:3'-methylenedicarbazole.

With nitrous acid (acetic acid and potassium nitrite) carbazole yields N-*nitrosocarbazole* m.p. 82° (Wieland, Annalen, 1912, **392**, 182).

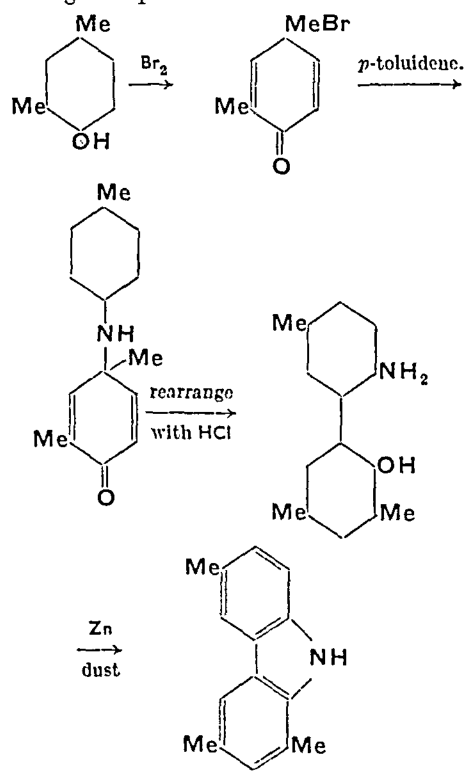
Potassium carbazole with carbon-dioxide is converted to potassium carbazole-N-carboxylate. This when heated in a stream of carbon dioxide at 270° yields carbazole-1-carboxylic acid (Briscoe and Plant, J.C.S. 1928, 1991), while at 285° the 2-carboxylic acid is formed (Plant and Williams, J.C.S. 1934, 1142). Above 300°C. or under pressure a carbazole dicarboxylic acid is produced.

(2) C-*derivatives.*—Carbazole or N-acylcarbazoles possess in general the reactivity of members of the benzene series and may be similarly nitrated, sulphonated or halogenated.

Usually substituents enter successively the 3, 6, 1, and 8 positions and then those remaining, but there are exceptions to this order.

Nitro-derivatives may be reduced to amino-compounds and thence converted, through the diazonium-salts, to nitriles, etc. Sulphonic-acid groups in carbazole may be replaced step by step with hydroxyl groups by means of caustic alkali (*e.g.* G.P. 580319). Remaining $-SO_3H$ groups may be removed by subjecting the product, for example, to the action of dilute acid at 180°C. under pressure (G.P. 258298). Carboxyl groups may be introduced into certain hydroxy carbazoles by the action of alkali and CO_2 (*e.g.* G.P. 586804).

Alkyl Carbazoles.—Alkyl carbazoles may be synthesised by the general methods given for carbazole itself. An example of another interesting mode of synthesis is illustrated by the following example :



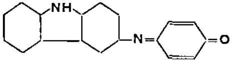
(Fries, Böker, and Wallbaum, Annalen, 1934, **509**, 73.)

According to U.S.P. 1972232 carbazole may be mono- and poly-alkylated with olefines under normal or increased pressure at 50°–200°C. using aluminium- or ferric-chloride as catalyst. Soft resinous materials are obtained by the reaction of carbazole with olefines in the presence of a hydrosilicate material with a large surface (U.S.P. 1916029).

Carbazyl Ketones.—In recent years the application of Friedel and Craft's reaction to carbazole has been the matter of several researches. It appears that unsubstituted carbazoles and N-alkyl carbazoles give 3 6 *diacylcarbazoles* with acyl halides and aluminium chloride. N-acyl carbazoles with $AlCl_3$ alone rearrange to the 3 acylcarbazoles, but in the presence of acyl-halide 2.9-diacyl compounds are produced (Plant, Rogers, and Williams, J.C.S. 1935, 741). On fusion with alkali the carbazyl-ketones yield the corresponding carboxylic acids (*e.g.* Plant and Williams, J C.S. 1934, 1142).

Uses.—The chief use of carbazole is as a dyestuff intermediate.

When carbazole is condensed with nitrosophenol in 80% sulphuric acid at a low temperature, carbazole indophenol,



is produced.

On heating this substance or its leuco derivative with sodium polysulphide the important dyestuff "Hydron-Blue" is formed (G.P. 218371).

Carbazole hydroxy sulphonic and carboxylic-acids, etc., may be used as secondary components in azo dyes. The tetrazo-compound from 3.6-diaminocarbazole, like other tetrazo compounds of benzidene derivatives, is used in the preparation of direct cotton dyes.

Pigments may be obtained by condensation of benzoquinone and carbazole derivatives, *e g.* of chloranil with 3-amino-N-ethyl-carbazole (B.P. 387565, 1933). *Certain anæsthetics are derived* from carbazole. The diethylaminoethyl ester of carbazole-N carboxylic acid, for example, is cited as a local anæsthetic ("carbacaine") (J. Pharmacol. 1933, 47, 69).

CARBAZOLE DYESTUFFS *v.* ANTHRAQUINONE DYESTUFFS.

CARBIDES. Carbon forms binary compounds, "carbides," with the majority of the elements. These compounds exhibit a remarkable range in their properties and methods of preparation: thus gold carbide, Au_2C_2 (also termed aurous acetylide), explodes when gently brushed from the filter paper on which it has been dried or when heated above 83° (Mathews and Watters, J. Amer. Chem. Soc. 1900, 22, 108), whilst the inert tantalum carbide, TaC, m.p. about 4,150° absolute, is extremely resistant to chemical attack and is one of the hardest artificial materials (Agte and Alterthum, Z. techn. Physik, 1930, 11, 18; Chem. Zentr. 1930, ii, 182). The preparation of heavy metal carbides in the electric furnace (Moissan, "The Electric Furnace," E. Arnold, London, 1904) may be contrasted with the method used by the same investigator for preparing pure carbides of sodium and potassium of which the first stage is the action of acetylene on the solution of the alkali metal in liquid ammonia at −40° (Compt. rend. 1898, 127, 917).

Occurrence.—Crystals of an iron carbide or *cohenite*, $(FeNiCo)_3C$, have been found in meteorites (E. Weinshenk, Ann. Mus Wien, 1889, 4, 94) and in the basalt of Ovifak (for a differing formula, *v.* 1928, A, 864). Moissanite, CSi (*cf.* carborundum), was found in a meteorite of Cañon Diablo, Arizona, by Moissan (Compt. rend. 1904, 139, 778; 1905, 140, 405; *cf.* Kunz, Amer. J. Sci. 1905, 19, 396). Natural carbides of heavy metals are of interest in connection with Mendeléef's theory of the origin of petroleum (Wagner, Ber. 1877, 10, 229; Mendeléef, "Principles of Chemistry," I, p. 403, Longmans, Green & Co, London, 1905). According to this theory water penetrating to depths where metallic carbides are subjected to high temperatures and pressures, will, by interaction, form gaseous and liquid hydrocarbons resembling those in crude petroleum. The considerable literature of the theory is summarised adversely, in Engler-Hoefer, "Das Erdoel," 1909, II, 62.

History.—H. Davy observed the properties of a product containing potassium carbide (Phil. Trans. 1809, 99, 39, 71). Edmund Davy made a quantitative examination of a crude potassium carbide, obtained by heating calcined cream of tartar with potassium carbonate, and of the gas generated from it by the action of water, but his correct determinations were overlooked for many years (Rep. Brit. Assoc. 1836, 62, 63; Trans. Roy. Irish Acad. 1839, 18, 80). Berthelot in the course of his researches on acetylene studied cuprous acetylide, Cu_2C_2, and its double salts (Ann. Chim. Phys 1863, [iii], 67, 52). Later he made the carbides of potassium and sodium by heating the metals in acetylene (*ibid.* 1866, [iv], 9, 385) Moissan, employing his electric furnace, prepared a large number of crystalline carbides by fusing a *metal or its oxide or carbonate* with charcoal (Compt. rend. 1894, 118, 501; *cf.* O. Hönigschmid, "Karbide und Silicide," W. Knapp, Halle/Saale, 1914; Moissan, "The Electric Furnace," *v.s.*). Although Moissan prepared in this way calcium carbide in 1892 its industrial manufacture arose independently in the U.S.A. (Willson, U.S.P. 492377, Aug. 5, 1892; *see* Vol. I, p. 106, and CALCIUM CARBIDE, this volume, p. 215). In 1890 Acheson, while endeavouring to crystallise carbon by dissolving it in fused aluminium silicate in an electric arc, obtained silicon carbide, SiC, *i.e.* carborundum (*q v.*; *see also* Chem. News, 1893, 68, 179; J. Franklin Inst. 1893, 136, 194, 279; 1903, 155, 465; B.P. 17911, 1892; 12221, 18339, 1893; 11473, 1895). A carbide of technical importance although not manufactured separately is cementite (*q.v.*), Fe_3C, hard crystals which form part of the structure of cast iron and steel; it was isolated by dissolving Bessemer steel in dilute sulphuric acid (F. Müller, Z. Ver. deut. Ing. 1878, 22, 456; Mylius, Foerster,

and Schoene, Z. anorg. Chem. 1897, **13**, 38). Following the discovery of the artificial abrasive carbide, carborundum, much attention has been given to electric furnace processes for the production of hard and refractory synthetic substances such as the carbides of boron (this vol., p. 44) and of titanium, tungsten, molybdenum, vanadium, tantalum, and zirconium. The last named carbides are used as constituents of iron-carbon alloys, containing also other metals, for the production of cutting tools superior to those of high-speed steel. Moissan had noticed the hardness of the carbides of molybdenum, tungsten, and chromium ("The Electric Furnace," p. 254) and Friederich called attention to this property in the case of the rare metal carbides (Fortsch. Chem. Physik. Physikal. Chem. 1926, **18**, 12). K. Becker discusses their manufacture and uses in "Hochschmelzende Hartstoffe und ihre technische Anwendung," 2nd ed., 1935, Verlag Chemie G.m.b.H., Berlin.

Non-metals.—One of the few remaining gaps in the list of carbides of the non-metals was filled by de Mahler's preparation of *phosphorus carbide*, P_2C_6, a white amorphous substance obtained by the action of phosphorus trichloride on Iotsitsch's compound, MgI·C:C·MgI (J.C.S. 1914, **106**, i, 393; de Mahler, Bull. Soc. chim. 1921, [iv], **29**, 1071). *Arsenic carbide*, As_2C_6, was also prepared.

Alkali Metals.—Guernsey and Sherman (J. Amer. Chem. Soc. 1926, **48**, 141) prepared pure white Na_2C_2 by the method of Berthelot (*l.c.*) at 220°, decomposition being avoided by adequate mixing of the melted sodium with the acetylene. With little water the compound liberates acetylene, but with a large excess an explosion occurs with deposit of carbon, and when ground in a mortar with sulphates or chlorides of the heavy metals explosive reactions take place. Treatment with iodine gives C_2I_4. Melted potassium inflames in acetylene; the pure carbide, K_2C_2, was prepared by Moissan (Compt. rend. 1898, **127**, 911) by heating *in vacuo* the precipitate obtained by passing acetylene into a solution of potassium in liquid ammonia cooled to −40°.

Magnesium Carbides.—Novák (Ber. 1909, **42**, 4209; Z. physikal. Chem. 1910, **73**, 513) by heating magnesium in acetylene to 400°–500° obtained mixtures of MgC_2 and Mg_2C_3, and a maximum of the latter compound at 545°. MgC_2 yields acetylene with water, but Mg_2C_3 gives allylene:

$$Mg_2C_3+4H_2O=2Mg(OH)_2+CH_3C{:}CH$$

Silver, copper, and mercury carbides are described in the article ACETYLENE, Vol. I, 82 l. Durand (Compt. rend. 1923, **177**, 693) mixed calcium carbide with cupric chloride solution and by treating the residue with dilute acetic acid obtained explosive cupric acetylide, CuC_2.

Gold. Aurous carbide, Au_2C_2, is precipitated when acetylene is passed into a strongly ammoniacal solution of aurous sodium thiosulphate, $Na_3Au(S_2O_3)_2$ (Mathews and Watters, *l.c.*). Au, Ag, and Cu do not form carbides when the metals are fused in contact with charcoal.

Lead. Plumbous acetylide, PbC_2, is contained in the grey precipitate given by calcium carbide in normal lead acetate solution (Durand, *l.c.*).

Beryllium carbide, Be_2C, from BeO and charcoal in an electric furnace (Lebeau, Compt. rend. 1895, **121**, 496) is harder than quartz and when treated with water evolves methane.

Zinc carbide, ZnC_2, an unstable white compound was obtained by the action of acetylene on zinc ethyl in light petroleum (Durand, Compt. rend. 1923, **176**, 992).

Aluminium carbide, Al_4C_3, from the elements at 2,000° in a hydrogen atmosphere. The best preparation contained 83% Al_4C_3 and 6·7% AlN. The gas evolved by treatment with hydrochloric acid contained 97·5% CH_4 (Ruff and Jellinek, Z. anorg. Chem. 1916, **97**, 312).

Iron, manganese, cobalt, and nickel carbides (for iron carbide, *v.* Cementite, Fe_3C, and Cohenite, *v. supra*; for hydrocarbons produced by acid hydrolysis, *v.* Mylius *et al.*, Ber. 1896, **29**, 2991). Carbides of these metals of the formula MC_2 have apparently been prepared in an impure state by Durand (*l.c.*). *Manganese carbide*, Mn_3C, crystals, hardness intermediate between talc and gypsum, was made by heating the elements at 1,600°. Hydrolysis yields equal volumes of hydrogen and methane (Ruff and Gersten, Ber. 1913, **46**, 400; J. Schmidt, Z. Elektrochem. 1934, **40**, 170). Cooling curves indicate the existence of Co_3C, but the compound decomposes before the melt solidifies (Ruff and Keilig, Z. anorg. Chem. 1914, **88**, 410). Similarly Ni_3C is very unstable when cooled from high temperatures (Ruff and Gersten, *l.c.*). *Titanium carbide*, TiC, was separated from cast iron by Shinner (Chem. News, 1887, **55**, 156). Moissan ("Electric Furnace," 1904, p. 254) prepared it as crystals which scratched diamonds. Its m.p. is 3,410° absolute, ±90° (Agte and Moers, *v. infra*). Carbides of Zr, Nb, Mo, Hf, Ta, W_2C, WC, very hard, refractory compounds, were studied particularly by Friederich and Sittig (Z. anorg. Chem. 1925, **144**, 169), Agte and Alterthum (Z. techn. Physik, 1930, **11**, 182; Chem. Zentr. 1930, ii, 700) and Agte and Moers (Z. anorg. Chem. 1931, **198**, 233) who heated the metals or their oxides with carbon in an inert atmosphere to 1,700°–2,100° and sintered the compressed material by electric heating (Agte and Moers). The latter authors prepared the carbides of Ti, Zr, Hf, V, and Ta by a growth method on a tungsten wire heated in an atmosphere of the metallic halide and hydrogen. SiC was also prepared in this way—yellow crystals without measurable electric conductivity. The m.ps. determined by Friederich and Sittig are in fair agreement with the following measurements of Agte and Moers.

	ZrC	NbC	Mo_2C	MoC
$t°$ absolute . .	3,808	3,770	2,960	2,965
*Hardness . .	8–9	+9	7–9	7–8

	HfC	TaC	W_2C	WC
$t°$ absolute . .	4,160	4,150	3,130	3,140
*Hardness . .	—	—	9–10	9

* Quartz = 7, topaz 8, corundum 9, diamond 10.

The uncertainty in the m p. is reported as Mo_2C, MoC, W_2C, WC, ±50° ; ZrC and NbC, ±125° ; HfC and TaC, ±150°. The carbides of hafnium and tantalum have the highest m p. yet observed. Technical applications of these refractories are discussed by Becker (*op. cit*). Theories of the structure of the metallic carbides have been proposed recently by J. Schmidt (*l c*) and by Schmahl (Z. Elektrochem 1934, 40, 68). According to the author first named, acetylene, is evolved by hydrolysing carbides whose crystal lattice contains the —C—C— linkage whilst the evolution of methane indicates that the carbon atoms are separated Moissan suggested a classification based on the gaseous products of hydrolysis (Compt rend 1896, 122, 1462; Z. Elektrochem. 1902, 8, 44) (For barium carbide, *v.* Vol. I, 637 r ; for calcium carbide, *v.* ACETYLENE, Vol I, 74 r, 107 l, and Vol. II, CALCIUM CARBIDE) J. N G.

CARBITOL. Diethyleneglycolmonoethylether (Carbide and Carbon Chemicals, New York).

CARBOHYDRASE. The general term given to the various specific enzymes which hydrolyse the carbohydrates.

CARBOHYDRATES. The term is applied to polyhydroxy-aldehydes and ketones, and to the substances which give these when hydrolysed by heating with mineral acids Glucose, sucrose, starch, and cellulose are carbohydrates universally distributed in plants. Glucose and glycogen enter into the composition of animal tissues. The simple carbohydrates, monosaccharides, have the empirical composition CH_2O, the most important being those containing 5 or 6 atoms of carbon. The complex carbohydrates, polysaccharides, are built up from two or more simple carbohydrates with the elimination of water , they have the composition $(C_6H_{10}O_5)_n,H_2O$. Compounds in which n equals 1, 2, 3, or 4 are distinguished by names having the suffix *-ose.* They may be conveniently grouped as follows :

1. Monosaccharides: $n=1$.
   (*a*) Pentoses, $C_5H_{10}O_5$, *e g.* arabinose, xylose.
   (*b*) Hexoses, $C_6H_{12}O_6$, aldoses, *e g.* glucose, mannose, galactose ; ketoses, *e g.* fructose, sorbose.
2. Oligosaccharides.
   (*a*) Disaccharides : $n=2$. $C_{12}H_{22}O_{11}$.
      (1) Non-reducing, *e g.* sucrose, trehalose.
      (2) Reducing, *e g.* maltose, lactose, etc.
   (*b*) Trisaccharides : $n=3$. $C_{18}H_{32}O_{16}$. Gentianose, raffinose, melezitose.
   (*c*) Tetrasaccharides : $n=4$. $C_{24}H_{42}O_{21}$. Stachyose.
3. Polysaccharides.
   (*a*) Glycogen, inulin, dextrins, n unknown.
   (*b*) Starch, cellulose, n large.

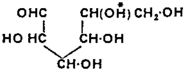
Related to the carbohydrates are those substances which yield simple carbohydrates, together with other substances when hydrolysed. Such are glycosides, gums, pectins, etc.

General Characters —The members of classes 1 and 2 are soluble in water. They have a more or less pronounced sweet taste. The monosaccharides are colourless crystalline compounds, characterised by the power of reducing alkaline solutions of the heavy metals, for example, copper. They form characteristic compounds with phenylhydrazine.

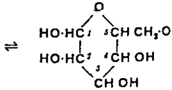
The di- and poly-saccharides are converted into simple carbohydrates when hydrolysed This change may be effected by means of mineral acids, or, as rule, more quickly by enzymes. The complicated polysaccharides are usually amorphous ; they tend to form colloidal solutions, and are chemically relatively inert. In virtue of the hydroxyl- groups which they contain, they react with acetyl chloride, benzoyl chloride, nitric acid, etc , forming esters

Carbohydrate solutions are generally optically active. The direction and amount of the rotation vary with the substance, and also with the strength of the solution, the nature of the medium, the temperature, etc. The optical rotatory power of carbohydrates is made use of in their analyses and as a guide to their structure

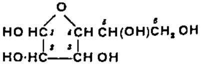
It is now recognised, largely as the result of the work of Haworth (" The Constitution of the Sugars," Arnold, London, 1929) that the stable forms of glucose possess a six-atom ring structure containing five carbon atoms and one oxygen, it is a 1.5 glucopyranose with a primary alcohol, $—CH_2·OH$, group as a side chain. One of the other hydroxyl groups represents the group which was originally the aldehydic group In fact, the transformation from the aldehyde form to the lactone form may be regarded as an instance of ring-chain tautomerism as indicated below, hence the occurrence of α- and β forms. On the other hand, the so called labile γ glucose and its derivatives contain a five-atom ring, and are represented as 1.4-glucofuranose with a longer side chain, $—CH(OH) CH_2 OH$.



Aldehyde form
(*Mobile hydrogen)



Glucopyranose
(α and β- forms)



Glucofuranose (γ- sugar).

In addition to these two ring forms of glucose, there exist derivatives of yet a third, a seven-ring or septanose, modification. Lastly there is evidence of a number of stable derivatives of the aldehydic form :

$$HO\,CH_2·[CH\,OH]_4·CHO$$

Thus the monosaccharides are known in the following forms :

6 atom rings	=pyranose.
5 ,,	=furanose.
7 ,,	=septanose.
Open chain	=aldehydo.

Glucose in solution can react in any of its four forms according to the reagents employed and the conditions of the experiment, so that the possibilities of isomerism are very large.

The validity of the butylene oxide ring formulæ adopted in the past mainly rested on the analogy with the lactones of the sugar acids : it has proved to be untenable.

The new structure is based on the belief that the ring system of methyl glucoside is not in any way modified by the usual processes of methylation, which if true makes it possible to determine the nature of the cyclic form by a study of the methylated lactone to which it gives rise.

However, whilst there is no question of a shift in the ring during the methylation of a gluco-pyranose derivative, the same cannot be said with certainty of a glucofuranose derivative, indeed with some compounds there is evidence to the contrary.

The Normal α- and β-Sugars of the Pyranose Series.

The α- and β-methylglucosides are converted by Purdie's original method (J.C.S. 1903, **83**, 1021, 1137), using silver oxide and methyl iodide, or by digestion in aqueous solution with methyl sulphate and alkali (Haworth, J.C.S. 1915, **107**, 8) into tetramethyl methylglucosides. Taking either the α- or β-form as example, their hydrolysis gives tetramethyl glucose, oxidation of this substance with bromine leads to tetramethyl-δ-gluconolactone and further oxidation with nitric acid to *i*-trimethoxy glutaric acid, which can be readily identified as its crystalline methylamide. The quantitative extent of the yields at each stage of this series of reactions shows that homogeneous substances are being dealt with. It cannot be too strongly emphasised that in determinations of structure dependence must be placed only on the isolation of definite crystalline substances which can be compared directly with known compounds of indisputable constitution.

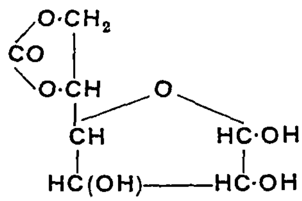
Labile γ-Sugars of the Furanose Series.

The labile γ-glucose itself has not yet been obtained crystalline, but Haworth and Porter (J.C.S. 1929, 2796) have obtained two ethylglucofuranosides. The proof of the γ-glucose structure (Haworth, Hirst, and Miller, J.C.S. 1927, 2436) lies in the series of facts that γ-glucose gives rise to a tetramethylglucose, differing markedly from the crystalline variety, which yields a crystalline tetramethyl-gluconolactone, differing sharply from the previously known compound of the pyranose series but having properties closely resembling those of ordinary γ-gluconolactone. Oxidation with nitric acid converts this lactone to di-O-methyl tartaric acid. It is inferred that the four-carbon chain of this acid represents the grouping of carbon atoms in the five-membered furanose ring.

The ethylglucofuranosides (Haworth and Porter, J.C.S. 1929, 2796) are prepared by condensation of glucose monoacetone with phosgene to give glucose acetone carbonate. Hydrogen chloride dissolved in ethyl alcohol removes the acetone group from this product with the formation of the α- and β-forms of the ethyl furanoside carbonate. Hydrolysis with barium hydroxide eliminates the carbonate grouping without displacement of the five-atom ring nucleus of the sugar.

	M.p.	$[\alpha]_D$
α-ethylglucoside 1:5 . .	113°	+150·6°
β-ethylglucoside 1:5 . .	73°	−36·5°
α-ethylglucoside 1:4 . .	82°	+98°
β-ethylglucoside 1:4 . .	59°	−86°

A further crystalline γ-sugar derivative is glucofuranose 5:6-carbonate,



which is obtained from the above-mentioned monocarbonate on removing the alkyl residue by hydrolysis with acids (Haworth and Porter, *l.c.*).

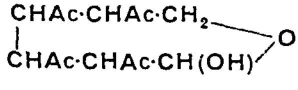
Crystalline α- and β-forms of pentabenzoyl-γ-glucose have been isolated by Schlubach and Huntenberg (Ber. 1927, **60**, [B], 1487). Their specific rotations (+58·6° and −52·6°) differ widely from those of the corresponding normal glucose derivatives (+107·6° and +23·7°) which agree fairly closely with those of α- and β-glucose (+110°; +17·5°). By analogy the rotations of α- and β-glucofuranose may be surmised, viz. the α-form will have a much lower positive value than α-glucopyranose, and the β-form will have a higher lævorotatory value than β-glucose.

Septanoses.

A 7-membered ring in the sugar series is obtained by reactions involving first the hydrolysis of 6-iodo-*d*-galactose mercaptal tetra-acetate with mercuric chloride and cadmium carbonate in the cold yielding the open chain 6-iodo-tetra-acetyl aldehydo galactose :

$$CH_2I{\cdot}[CH{\cdot}OAc]_4{\cdot}CHO$$

At 40° the iodine is removed and the open chain hydrate formed. In pyridine solution non-reversible ring closure occurs and the cyclic sugar tetra-acetyl-*d*-galactoseptanose is formed :



A separable mixture of α- and β-*d*-galacto-septanose penta-acetates is obtained from this

on acetylation (Micheel and Suckfüll, Annalen, 1933, 502, 85 ; 507, 138).

The stability of the septanose ring is of the same order as that of the furanose ring (Micheel and Suckfüll, Ber. 1933, 66, [B], 1957).

Hydrolysis of either penta acetate with weak alkali yields pure galactopyranose.

Glucose as an Aldehyde.

Two methods are available for the preparation of open chain monosaccharides. They take advantage of the opening of the pyranose ring which occurs when the sugars are condensed with (a) ethyl mercaptan, (b) hydroxylamine.

Penta-methyl derivatives of glucose, mannose, and galactose were prepared by Levene and Meyer (J. Biol. Chem. 1926, 69, 175) in aldehydic form by methylation of the corresponding diethyl mercaptal followed by hydrolysis of the mercaptal group. Better characterised are the crystalline acetates and benzoates.

The crystalline 2·3 4 5 6 penta-acetylglucose (Wolfrom, J. Amer Chem Soc 1929, 51, 2188) has a rotation nearly zero and gives a positive test with Schiff's reagent Penta-acetylgalactose (Wolfrom, *ibid* 1930, 52, 2462) and tetra acetyl-*l* arabinose (Wolfrom and Newlin, *ibid.* 1930, 52, 3619) have rotation values in chloroform of −25° and −65° respectively ; they have been synthesised from the dimethylmercaptals of the sugars. Aldehydopentabenzoylglucose has likewise been prepared (Brigl and Muhlschlegel, Ber. 1930, 63, [B], 1551).

A further aldehydoacetate is that of xylose, m p. 87°, $[\alpha]_D$ −16° (Wolfrom, J. Amer Chem. Soc. 1931, 53, 4379). The aldehydoacetates have the following constants ·

Sugar	M p	$[\alpha]_D$
d-glucose penta-acetate	116°	−4 5°
d galactose penta acetate	121°	−25°
l-arabinose tetra acetate	114°	−65°
d-xylose tetra acetate . .	87°	−16°

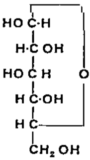
An open chain structure is also assigned to the phenyl and other hydrazones of galactose (Wolfrom and Christman, *ibid.* 1931, 53, 3413, *cf. also* Frèrejacque, Compt rend 1925, 180, 1210).

Aldehydo *l* glucose tetra acetate has been made by Wolfrom and Orsino (J. Amer. Chem. Soc. 1934, 56, 985).

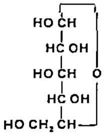
A method developed for distinguishing between open chain and cyclic acetates consists in treating the acetate with ethyl mercaptan in the presence of zinc chloride ; the open chain compound so treated yields a mercaptal containing the same number of acetyl groups, whereas the cyclic compound gives a thioethyl derivative with one acetate less (Wolfrom and Thompson, *ibid.* 1934, 56, 880, 1804 ; Brigl and others Ber. 1931, 64, [B], 2932 ; 1933, 66, [B], 325)

The acetylation of sugar oximes leads to a mixture of three products—thus from galactose oxime there results aldehydogalactose oxime hexacetate and an isomeride, also galactonitrile penta acetate. The first on treatment with nitrous acid gives aldehydogalactose penta-acetate, which is easily separable from the nitrile (Wolfrom and others, J. Amer. Chem. Soc. 1933, 55, 3488 ; 1934, 56, 1794). The method allows of the synthesis of the open chain acetates of those disaccharides and ketoses the thioacetates of which are not available.

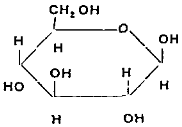
The extension of the classic open chain sugar formulæ introduced by Emil Fischer to cyclic sugar formulæ involves an error in the configuration of the groupings at C_5 in the glucose formula (I). The act of ring closure from an open chain to a cyclic form causes the rotation of the linking between C_5 and C_6 through 120°, which has the effect of bringing the H at C_5 on the opposite side of the carbon chain as is correctly expressed in formula II. Haworth now uses a perspective formula (III) which is even more satisfactory, and it is likely to enter into general use ; it shows the groups above and below the plane of the ring.



I.

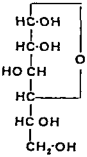


II.

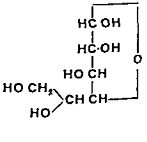


III.

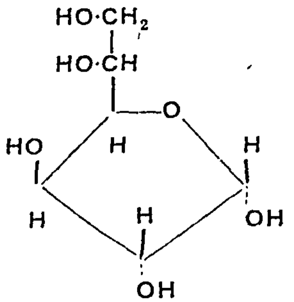
A corresponding correction has to be made for all the other sugars, and also for glucofuranose (*see* Josephson, Ber. 1929, 62, [B], 317, 1913), the respective formulæ for which are :



IV.



V.



VI.

Formula VI illustrates the spatial proximity of the OH groups at C_3 and C_6 and helps to account, for example, for the wandering of an acyl residue which takes place between C_3 and C_6 in monoacetyl glucose derivatives.

Interesting generalisations have been drawn by Hudson concerning the molecular rotations of α and β forms of sugars. It is now generally accepted that the difference between the molecular rotations of the α and β forms of mutarotatory sugars is a constant. The compounds selected show considerable diversity of type and discordant results have from time to time been explained away by showing that the compound in question is derived from other than the α and β forms of the sugar (*cf.* Hudson, J. Amer. Chem. Soc. 1917, 39, 1013). The maximum values for the specific rotations are now arrived at by the indirect method based on solubility measurements (Lowry, J.C.S. 1904, 85, 1551 ; Hudson, J. Amer. Chem. Soc. 1904, 26, 1065). The asymmetric system attached to the α-carbon atom exerts a preponderating influence on the activity of these compounds and determines the sign of the rotation.

Hudson's generalisation has enabled the optical rotatory power of carbohydrate derivatives to be used as an important guide to their structure.

Constitutional Formula of Glucose.—In addition to those carbohydrates which occur naturally, a number of others have been prepared artificially by Emil Fischer, and it is largely to his work that the present complete knowledge of the group is due. (Fischer's original work has been republished, "Untersuchungen über Kohlenhydrate," Berlin, 1909, J. Springer.)

Glucose and its isomerides, $C_6H_{12}O_6$, conveniently termed glucoses, have 5 oxygen atoms present as "hydroxyl," since they form esters such as glucose pentacetate,

$$C_6H_7O(O{\cdot}CO{\cdot}CH_3)_5$$

The sixth oxygen is aldehydic in glucose and galactose, and ketonic in fructose and sorbose. The two classes of compounds are accordingly referred to as aldoses and ketoses. Reduction converts the glucoses into alcohols, $C_6H_{14}O_6$, glucose yielding sorbitol and mannitol, and galactose forming dulcitol. Secondary hexyl-iodide, a derivative of normal hexane, is formed by the action of hydrogen iodide ; hence the glucoses must possess all their six carbon atoms united in normal chain.

Glucose on oxidation yields, in the first place, gluconic acid, $C_5H_6(OH)_5CO_2H$, which retains all six carbons and, like glucose, forms a pentacetyl ester. Further oxidation converts it into saccharic acid, $C_6H_{10}O_8$. Galactose behaves similarly, yielding the isomeric galactonic and mucic acids. Taking further into consideration the reducing power of glucose, the constitutional formula may be written :

$$CH_2(OH)CH(OH)CH(OH)CH(OH)CH(OH)CHO$$

The work of Tanret (Compt. rend. 1895, 120, 1060) has shown that glucose exists in more than one form. In addition to the hydrated and anhydrous modifications, he isolated two other anhydrous modifications. These differed particularly in optical rotatory power. Tanret described an α-glucose having $[\alpha]_D$ +110° when first dissolved, and falling in aqueous solution ; a β-glucose having $[\alpha]_D$ +19°, and increasing in solution ; and a glucose having $[\alpha]_D$ +52·5°, and remaining constant in solution. This modification was called γ-glucose by Tanret. It had long been known that the optical rotatory power of freshly dissolved glucose diminished to about one-half its initial value in solution, and the term *mutarotation* or *birotation* was applied to this phenomenon.

Dubrunfaut ascribed the change to purely physical causes. Fischer considered that the aldehyde dextrose underwent hydration to an alcohol, $C_6H_{14}O_7$, of lower rotatory power. In view of Tanret's discoveries, it is now considered that the change in rotatory power is due to the mutual interconversion of the α- and β-glucose until equilibrium is attained. Tanret's γ-glucose represents such an equilibrium mixture.

To understand fully the relation of α- to β-glucose, it is necessary to refer to the van't Hoff-Le Bel conception of space isomerism. Chemical compounds which rotate the plane of polarised light contain an *asymmetric carbon atom*, that is, one in which the four affinities are satisfied by four different radicals. Such a carbon atom is considered as lying in the centre of a tetrahedron, and each of the four different radicals with which it is combined as being at the four solid angles thereof. Two modifications of the compound are possible, and these are related to one another as an object and its reflected image.

The compound represented by the formula

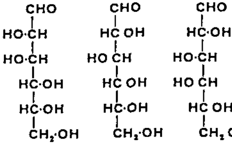
$$CH_2(OH)\overset{*}{C}H(OH)\overset{*}{C}H(OH)\overset{*}{C}H(OH)\overset{*}{C}H(OH)CHO$$

contains four asymmetric carbon atoms (marked *), and should, therefore, be capable of existing in 16 stereoisomeric forms, 8 of which would be mirror images of the other 8, and of equal but opposite rotatory power.

The carbohydrate group has afforded a unique opportunity of testing this hypothesis, and although only three of the isomerides occur naturally, all 16 have been prepared artificially by Fischer and others, by such methods that the structure of each is established.

The known aldohexoses are the *dextro-* and *lævo-* isomerides of mannose, glucose, idose,

gulose, galactose, talose, allose, and altrose. It will suffice to give the constitutional formulæ as established by Fischer of the naturally occurring members :



Mannose. Glucose Galactose

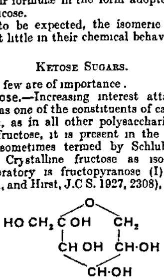
Mannose and galactose, like glucose, exist in α- and β- forms, and it is more correct to write their formulæ in the form adopted for α- and β-glucose.

As is to be expected, the isomeric glucoses differ but little in their chemical behaviour.

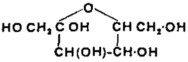
Ketose Sugars.

Only a few are of importance.

Fructose.—Increasing interest attaches to fructose as one of the constituents of cane sugar in which, as in all other polysaccharides containing fructose, it is present in the labile or γ form, sometimes termed by Schlubach the λ-form. Crystalline fructose as isolated in the laboratory is fructopyranose (I) (Avery, Haworth, and Hirst, J.C.S. 1927, 2308),

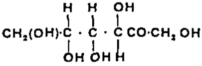


I.



II.

but there is a growing doubt as to whether the labile γ-form is fructofuranose (II), and there is a considerable support for the keto formula—



For example, as Hudson has pointed out, sorbose and other ketoses exist in one form only and do not exhibit mutarotation. Moreover, there is no tendency for the acetates of fructose to isomerise. The mutarotation of fructose may, therefore, be due to the simple opening of the ring.

Ordinary fructose is the β form $[\alpha]_D$ $-132.5°$, which mutarotates very rapidly into the equilibrated mixture $[\alpha]_D$ $-92.5°$. Heat is absorbed during the change.

As a commercial sugar fructose offers great possibilities because of its sweetness. When the chemical engineering problems involved in its isolation on a large scale are solved, it may well become an important commercial product.

Desiccated tubers of the Jerusalem artichoke are being used for its manufacture to the extent of 50 lb. per day at one experimental plant. The sugar is isolated as the insoluble compound it forms with lime.

Inulin is easily hydrolysed under pressure (Arsem, U.S.P. 1763080) by water containing CO_2 or SO_2.

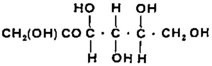
Anhydrides of fructose are contained in sinistrin, the carbohydrate from the bulbs of *Scilla Maritima* (Schlubach and Florsheim, Ber. 1929, 62, 1491), viz. di- and tetra-fructose anhydrides, whilst rye flour contains 1% of a trifructose anhydride (Tillmans, Holl and Jariwala, Z. Unters Lebensm. 1928, 56, 26).

Sorbose (sorbinose), $C_6H_{12}O_6$, is the ketohexose obtained from the juice of the mountain ash berries, which has been exposed to the air and allowed to ferment. The juice contains sorbitol ; this is oxidised by *bacterium xylinum* to sorbose.

Sorbose forms rhombic crystals of a sweet taste, m.p. 154° ; it reduces Fehling's solution, and generally behaves as lævulose, but yields sorbitol on reduction. It is not fermentable by yeasts. It is lævo rotatory, having $[\alpha]_D$ $-42°$.

Sorbose phenylosazone is similar to the glucose compound, but has m.p. 164°.

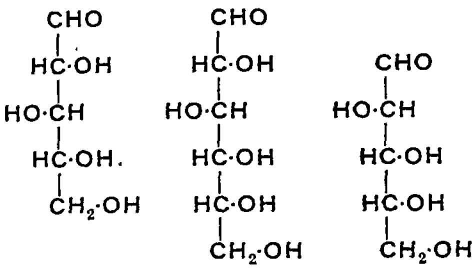
The properties are in agreement with the structural formula :



The first example of a diketose has been prepared by Micheel and Horn (Annalen, 1934, 515, 1) starting from di-iodo dimethylene mannitol. It reduces Fehling's solution in the cold, forms crystalline phenylhydrazones and osazones, and is remarkable in being fermented by yeast. The natural ketoheptoses are *d*-mannoketoheptose present in the Avocado pear ; perseulose, which is *l*-galaheptose ; and sedoheptose obtained from *Sedum spectabile*.

Pentoses, $C_5H_{10}O_5$.

These are widely distributed in plants, where they are present in the skeletal structure, and do not, like the hexoses, serve as food products. Pentoses also appear to be a constituent of many of the tissues of the animal body, and are sometimes found in urine. Both the natural pentoses, *l*-arabinose and *l*-xylose, belong to the *lævo*- series. Glucose, when degraded by the methods of Ruff or Wohl, gives rise to the isomeric *d*-arabinose. However, the natural pentoses are closely related to the natural hexoses. For example, the space arrangement of the groups attached to the upper four carbon atoms is the same in *d*-glucose as it is in *l*-xylose :



l-Xylose. *d*-Glucose. *d*-Arabinose.

A similar relationship exists between galactose and arabinose, which occur together in many gums, whilst some polysaccharides yield both xylose and glucose on hydrolysis. The pentoses do not occur as such in plants, but in the form of condensation products of high molecular weight, termed "pentosans" (araban or xylan). These are comparable with the hexose condensation products, starch and cellulose; as a rule, the pentosans contain both pentose and hexose carbohydrates.

The mechanism of the formation of pentoses in the plant is not yet clear. Some authorities consider they are derived by oxidation from the hexoses; others advocate the view that they are directly formed in the cell, like the hexoses, but independently of these. Such a transformation as that from glucose to *l*-xylose has not been effected in the laboratory: the chemical degradation of glucose by oxidation leads to *d*-arabinose. The pentoses show all the general chemical properties of the hexoses. *Biochemically* they are different, being not fermentable by yeasts, whilst their glucosidic derivatives (*e.g.* the methyl arabinosides and xylosides) are not hydrolysed by any of the better-known plant enzymes. They are attacked by a number of bacteria. Characteristic of the pentoses is the formation of furfurol on distillation with hydrochloric acid. They therefore show colour reactions with orcinol and phloroglucinol. It is now considered that pentoses are not primary products of photosynthesis but derived from the hexoses via glucuronic acid which is formed as the result of oxidation of the $—CH_2·OH$ group of glycosides. Glucuronic acid in sunlight, for example, splits off carbon dioxide to yield xylose.

d-Ribose, the pentose of the nucleosides of plants and animals, is to-day in the forefront of interest. It was first isolated by Levene and Jacobs, and its structure has been proved by synthesis. It is the pentose corresponding to *d*-allose and *d*-altrose.

A furanose structure has been allotted to the ribose residues in the nucleosides (Bredereck, Ber. 1933, 66, [B], 198).

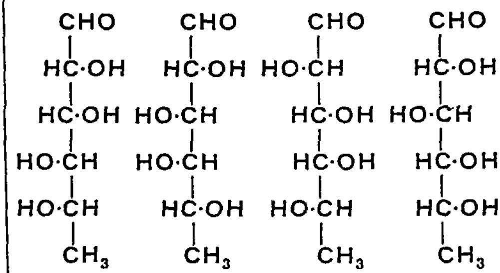
The nucleotides consist of phosphoric acid and a purine base united by ribose. For example, according to Gulland and Holiday (J.C.S. 1936, 765) adenylic acid is adenine-9-riboside-5-phosphoric acid.

Ribose is also a component of lactoflavin, which is vitamin B_2 being united to the complex nitrogenous compound lumiflavin (*see* Karrer and others, Ber. 1935, 68, [B], 216).

The Methyl Pentoses.—Most of the queries in this group have been cleared up as the result of the work of Votoček and his pupils (Bull. Soc. chim. 1928, [iv], 43, 1) and of Freudenberg and Raschig (Ber. 1928, 61, [B], 1750; 1929, 62, [B], 373). The former has proposed a systematic nomenclature by suffixing the term "methylose" to the name of the corresponding hexose. Thus *l*-rhamnose is *l*-manno-methylose. The names rhamnose and fucose are retained, also epirhamnose and epifucose. The name rhodeose, which is *d*-fucose, is abandoned. Chinovose (quinovose), the sugar component of α- and β-chinovin, has been shown to be *d*-epirhamnose (Freudenberg and Raschig, *l.c.* Votoček and Rác, Coll. Czech. Chem. Comm. 1929, 4, 239).

Ten methylpentoses have in all been obtained synthetically, four of them occur in plants.

The four natural methylpentoses are:



l-(+) rhamnose =*l*-manno-methylose. *d*-(+) fucose =*d*-galacto methylose. *l*-(−) fucose =*l*-galacto methylose. *d*-(+) epi-rhamnose.

The signs in brackets indicate the direction of the rotation.

The method of origin of the methylpentoses in plants is still obscure. *l*-Rhamnose, which is perhaps the commonest, has the same configuration as *l*-mannose, and hence cannot be derived from *d*-glucose or *d*-mannose by a simple process of reduction. Freudenberg and Raschig (Ber. 1929, 62, [B], 373) suggest the natural hexitols as a possible source, and they derive *d*-epirhamnose from sorbitol, *d*- and *l*-fucose from dulcitol. But *l*-rhamnose cannot be derived in this way from *l*-mannitol.

The synthetic methylpentoses are:

d-(−) mannomethylose or *d*-rhamnose.
d-(−) gulomethylose.
d-(+) talomethylose or *d*-epifucose.
l-(−) altromethylose.
l-(−) glucomethylose or *l*-epirhamnose.
l-(−) talomethylose or *l*-epifucose.

The (+) or (−) sign is used to indicate the direction of the rotation.

Each pair of methyloses give a common phenylosazone; these have been isolated and characterised:

Pair.	$[\alpha]_D$.	m.p.
d-allo and altro	−75°	185°
d-gluco and manno . . .	−77°	191°
d-gulo and ido	left	140°
d-galacto and talo . . .	+70°	178°

The methylpentoses are not fermented by yeasts; their biological significance is not yet understood.

The accepted rotation values for the mutarotatory sugars are given in the table. A fuller table with references to the literature will be found in Vogel and Georg ("Tabellen der Zucker und ihre Derivate," Berlin, 1936).

Sugar	α	Rotation Constant value	β
Glucose	111 2°	52 2°	19 2°
Galactose	144 5°	81°	52 2°
Mannose	30°	14 6°	−14°
Fructose	—	−93°	−133°
Sorbose . .	—	42 9°	—
Xylose	92°	19°	—
l Arabinose	175°	105°	55·4°
l Rhamnose	30 2°	10 1°	—
l Fucose	—	−75 3°	−93°
Lactose	90°	55 3°	35°
Maltose .	—	136°	118°
Cellobiose .	—	35°	16°

Sweetness and Bitterness of the Sugars.

The relative sweetness of the various sugars has been determined by Biester, Wood, and Wahlin (Amer. J. Physiol. 1925, 73, 387) on the basis of sucrose=100.

Sucrose . .	*100*	*Maltose* .	*32 5*
Fructose .	173	Rhamnose	32 5
Invert sugar	130	Galactose	32
Glucose	74	Raffinose	22
Xylose .	40	Lactose .	16

They find that invert sugar=130 when prepared by hydrolysis and =127 4 when made by the use of invertase

A number of sugar derivatives of solubility varying from 4% to 0 00125%, and of different bitterness to taste compared with glucose pentaacetate as a standard, have been investigated stalagmometrically by Brigl and Scheyer (Z. physiol. Chem. 1926, 160, 214). There is no direct relationship between surface activity and degree of bitterness; the greatest bitterness is possessed by sucrose octa acetate, 34×10^{-6} g. *being detectable by taste. All the derivatives of β-glucose are more bitter than those of α-glucose.* α-Mannose tastes sweet, β-mannose has a bitter after-taste (Hudson and Sawyer, J. Amer. Chem. Soc. 1917, 39, 474)

The Deoxy Sugars.

Considerable interest attaches to the reduced or 2-deoxy sugars, since they have been identified as natural products. *d*-Ribodesose occurs in nucleic acids. Digitoxose is the sugar of the digitalis glycoside digitoxin (Kiliani, Ber. 1905, 38, 4040). All are unstable and their crystals on *standing become a coloured tar. A characteristic* test devised by Kiliani (Arch. Pharm. 1913, 251, 567) is that when dissolved in glacial acetic acid to which sulphuric acid containing ferrous ions is gradually added, a blue or purplish-blue colour is developed. They do not form osazones.

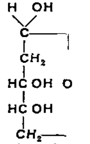
Synthetically they are prepared from glucal by treatment with cold dilute sulphuric acid (Bergmann, Schotte, and Lechinsky, Ber. 1922. 55, [B], 188).

They are more reactive than the simple sugars, the glycoside being readily formed and rapidly decomposed. They have been proved to have a pyranose structure (Bergmann and Breuers, Annalen, 1929, 470, 38; Levene and Mikeska, J. Biol Chem. 1930, 88, 791).

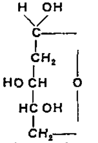
They are readily converted by the action of mineral acids into levulinic acid (Levene and Mori, J. Biol. Chem. 1929, 83, 803).

There are only 2 deoxy pentoses possible, viz 2 deoxy-ribose and xylose and their anti*podes. The d form of the former, sometimes* called thyminose, prepared by Levene (J. Biol *Chem. 1929, 85, 785), has m.p. 78°C.,* $[\alpha]_D$ in water +50°, the phenylhydrazone has m p. 128°–130°C., $[\alpha]_D$ −17·5°.

The synthetic *d*-xylodeose has m.p. 92°C, $[\alpha]_D$ −2°, *the phenylhydrazone has m p.* 116°–118°C., $[\alpha]_D$ +13 5°.



2-deoxy ribose.



2 deoxy-xylose.

2 deoxy *l* ribose (also called *l*-deoxyarabinose) is obtained from *l* arabinal (Meisenheimer and Jung, Ber. 1929, 60, 1462).

There remain for mention certain other sugars which are described in detail elsewhere. *Apiose*, the sugar of the flavone glycoside apiin found in parsley, has a branched chain of carbon atoms,

$$(CH_2OH)_2C(OH)CH(OH)CHO$$

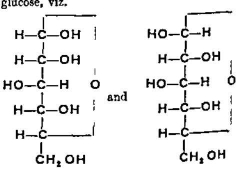
Hamamelose, found in a tannin, attached to 2 mols. of gallic acid has the structure

$$CH_2(OH)CH(OH)CH(OH)C(OH)\left<\begin{matrix}CH_2OH\\CHO\end{matrix}\right.$$

Digitoxose is a reduced or deoxy methylpentose Cymarose present *in Canadian hemp is regarded* as its methyl ether and is isomeric with sarmentose, a constituent of *Strophanthuss armentosus Digitalose* is regarded as a methoxy methyl pentose.

The Configuration of α- and β Glucose.

The respective space formulæ of α- and β glucose, viz.



have been established in a number of different ways in particular by Böeseken (Ber. 1913, 46, 2612 ; Rec. trav. chim. 1921, 40, 553) whose choice is based on the fact that the conductivity of boric acid in presence of a α-glucose decreases during mutarotation, showing that the sugar possesses two adjacent hydroxyl groups on the same side of the carbon chain, and again more recently by Riiber (Norske Videns, Selskabs, 1931, 4, 157), who finds that the molecular refractivity for *D*-light of α-glucose is 62·68, and of β-glucose is 63·07. This is in agreement with the general rule that a compound containing two neighbouring groups in the *trans-* position has a higher molecular refractivity than the corresponding *cis-* form.

Another physical proof of the structure is the observation of Michaelis (Ber. 1913, 46, 3683) that the β-methylglucoside has a higher dissociation constant than α-glucose, the separation of the OH and OCH_3 groups being accompanied by an increase in acidity.

Considered from the more purely chemical side the formulæ chosen are in harmony with the easy preparation of α-glucosan with an ethylene oxide structure from α-glucose indicating the presence of *cis*-hydroxyl groups and of β-glucosan from β-glucose. The structure of both these glucosans has been proved in quite another manner.

Glucose in Solution.

The question as to the number of isomeric forms of glucose which may be present in an ordinary aqueous solution is an open one. It is generally postulated that the α- and β-pyranose, the α- and β-furanose, and the aldehydic form can all be present, to which must now be added perhaps the septanose form. The aldehyde is the intermediate form from which they are all derived and through which they can all be converted into one another (*cf.* Lowry, Z. physikal. Chem. 1927, 130, 125).

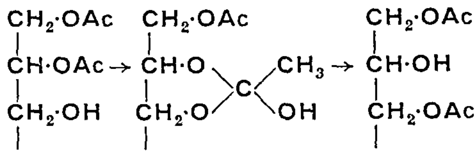
Interconversion of α- and β-Glucose Derivatives.

It is characteristic of the sugars that they are prone to undergo interchange of the groups on an asymmetric carbon. This particularly applies to the groups attached to carbon 1 in gluco-pyranose, and to a less extent to those attached to carbon 2. This latter change is exemplified by the conversion of glucose into mannose in presence of alkali and of gluconic acid into mannonic acid on heating with pyridine ; the reaction is often spoken of as *epimerism*. A rearrangement on the other carbon atoms is unusual.

The methods for the interconversion of α- and β-glucose derivatives are of interest. That of the hexosides is possible by digestion with methylalcoholic hydrogen chloride. β-Forms are converted readily into α-forms in non-ionising solvents containing stannic chloride (Pacsu, Ber. 1928, 61, [B], 137, 1508). Tetra-acetyl-β-methylglucoside is smoothly converted into the α-variety in presence of titanium tetrachloride, but under similar conditions β-glucose penta-acetate is transformed into α-chlorotetra-acetylglucose. The conversion of the α-chloro-tetra-acetylglucose to the β-compound only requires 8–10 minutes in the presence of an active form of silver chloride (Schlubach, Stadler, and Wolf, Ber. 1928, 61, [B], 287).

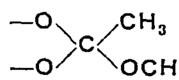
The possibility of a change from α to β must always be borne in mind when effecting any reaction in this group. Indeed, as is witnessed by the very extensive literature on the subject, it more often happens than not.

As a rule, substituting groups on any particular carbon are stable, but some interest has been attracted by the wandering of acyl groups linked with polyhydric alcohol residues, which was first observed by Emil Fischer (Ber. 1920, 53, [B], 1624), who suggested the intermediate formation of an orthocarbonic ester group :



This explanation applies both to the simple migration from carbon 3 to carbon 6, and also from carbon 1 to carbon 6 in the conversion of 1:2:3:4-tetra-acetyl β-glucose into the 2:3:4:6-tetra-acetyl derivative (*see* Josephson, Ber. 1929, 62, [B], 317, 913 ; Oldham, J.C.S. 1925, 127, 2840 ; Fischer and Delbrück, Ber. 1909, 42, [B], 2778; Helferich and Klein, Annalen, 1927, 455, 173 ; Helferich, Ber. 1930, 63, [B], 2142).

A similar explanation probably applies to the formation of anomalous so-called third forms of triacetylmethylrhamnoside, tetra-acetylmethylmannoside, and hepta-acetylchloro-maltose, for which at one time a novel form of stereoisomerism was assumed. The resistance to hydrolysis of one of the acetyl groups is attributed to its participation in the complex



(*see* Chem. Soc. Annual Reports, 1930, 104, for a fuller discussion and references).

Compounds of the Sugars with Ketones and Aldehydes.

The acetone compounds of the sugars are of particular value since they are used as the starting point for the preparation of partly substituted derivatives—acetates, benzoates, methyl ethers—which in turn are required for syntheses of various kinds. The condensation of acetone with monosaccharides usually involves *cis*-hydroxyl groups at contiguous carbon atoms ; a transformation of the pyranose to the furanose form takes place when such a transformation makes two *cis*-hydroxyl groups available. In exceptional instances the hydroxyl groups at carbon 4 and carbon 6 are brought into such spatial proximity as to be equivalent to a pair of *cis*-hydroxyl groups (*see* Haworth and others, J.C.S. 1935, 1012 ; 1926, 611 ; *also* Ohle and Vargha, Ber. 1929, 62, [B], 2425 ; Reichstein and Grüssner, Helv. Chim. Acta, 1934, 17, 311).

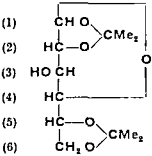
With aldehydes—*e g.* benzaldehyde—the substituted methylene ether most readily formed is that with a six membered ring, *e g.* 4:6 monobenzylidene glucopyranose (Zervas, Ber. 1931, 64, [B], 2289).

Acetaldehyde more nearly resembles benzaldehyde than it does acetone in condensing with the sugars. The acetone derivatives are formed when the finely divided sugar is shaken in *acetone suspension in the presence of a small* amount of hydrogen chloride, zinc chloride, or anhydrous copper sulphate. Many of them are crystalline. They are stable to alkali but unstable in the presence of dilute acid. Glucose forms a well defined diacetone compound (I) with a free hydroxyl at carbon 3. It is converted into a 3 monomethylglucopyranose though itself it has a furanose structure. The mono acetone obtained on hydrolysis can be converted into a 3:5.6-trimethylglucofuranose (for references and a fuller account see "The Sugars," by Haworth, London, 1929).

Normal fructose forms two crystalline diacetones. The one (II) is a fructosepyranose, and *so is the 3 monomethyl derivative obtained* from it. The other (III) has the terminal position carbon 1 exposed and is also a pyranose. Galactose gives rise to a diacetone (IV), which is also a pyranose. Its 6-iodohydrin is reduced to fucose diacetone.

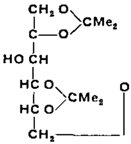
Acetone Compounds of :

γ-Glucose

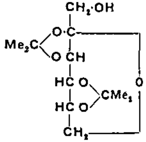


I.

Normal Fructose



II. (α form)

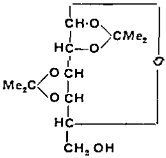


III. (β form)

The crystalline diacetone of mannose (V) displays mutarotation ; it is a furanose compound. A 5-atom ring is also present in xylose diacetone (VI), but here the atoms at alternate carbons are involved in the union with acetone. Owing to the configuration of xylose, which is brought out by writing the formula with carbon 5 as a side chain (VII), the third and the fifth hydroxyl groups are brought into such spatial proximity that the distance is equal to that between *cis* hydroxyl groups on neighbouring carbon atoms.

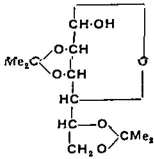
Acetone Compounds of :

Galactose



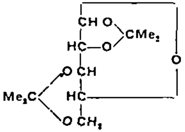
(Normal) IV.

Mannose

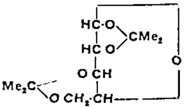


V. (γ-form)

Xylose.



VI.



VII.

It is clear from these results that acetone residues condense with appropriately situated hydroxyl groups in a sugar regardless of any preformed ring system in that sugar. The sugar ring adjusts itself to the position left open after the acetone residues are attached; for example, a shift of the position of the ring takes place in glucose, mannose, and xylose. This conception of the shift of the ring is important; it may equally well happen with other reagents besides acetone.

These acetone compounds are of utility in synthetic operations in that they mask certain groups during such reactions as methylation or acetylation, which groups are rendered subsequently available on removal of the *iso*propylidene residue.

Glucose, galactose, and the glucosides all combine with triphenylmethylchloride, forming triphenylmethyl ethers attached to carbon 6. These ethers are hydrolysed by alkali hydroxide as well as by hydrochloric acid, so that they afford a means of obtaining glucose derivatives with a free hydroxyl group on carbon 6, and from this a 6-monomethylglucose (Helferich and Becker, Annalen, 1924, **440**, 1; Helferich, Moog, and Jünger, Ber. 1925, **58**, [B], 872).

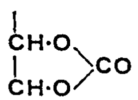
Triphenylmethyl-α-*d*-glucose (+2EtOH) has m.p. 57°–58°, $[\alpha]_D$ +59·6°, falling to +38° in pyridine.

Triphenylmethyl-*d*-galactose (+EtOH) has m.p. 73°–75°, $[\alpha]_D$ +0·58°, rising to +2·24° in pyridine.

The hydroxyl on carbon 6 of glucose displays a number of special reactions, in particular combination with *p*-toluenesulphonyl residues. The alkaline hydrolysis of such an ester leads, when a second hydroxyl group is available, to the formation of an anhydro ring which may then be ruptured by further and more drastic treatment with alkali. Both reactions—the formation of the anhydro-ring and its rupture by alkali—are usually accompanied by a Walden inversion (*see* Ohle and others, Ber. 1928, **61**, [B], 1211; 1933, **66**, [B], 525; 1935, **68**, [B], 601; *also* Robertson and Griffith, J.C.S. 1935, 1193; Oldham and Robertson, *ibid.* 1935, 685, likewise summary in Chem. Soc. Annual Reports, 1935, 280).

It is not yet possible to say whether anhydro-ring formation is a necessary concomitant of Walden inversion or whether simple hydrolysis of the toluenesulphonyl group is sufficient to induce inversion. Walden inversion in the sugar series has also been produced by means of aluminium chloride (Chem. Soc. Annual Reports, 1926, 90).

Sugar Carbonates.—Haworth and Porter (J.C.S. 1930, 151) have prepared crystalline dicarbonates of the sugars containing two residues of the type



which resemble closely the diacetone derivatives, but are not so readily hydrolysed by dilute acids; they are assigned similar structural formulæ:

	M.p.	$[\alpha]_D$ in acetone.
Glucose dicarbonate .	224°	−29°
Galactose	212°	−86·5°
Mannose	122°	+26°
Fructose	173°	−143°
Arabinose	200°	+61°

The carbethoxy derivatives (Zemplén and László, Ber. 1915, **48**, 921) are of the same type as the penta-acetyl compounds, each —OH being substituted by $—O·CO·OC_2H_5$.

The Methylo-Glucoses.

These are true ethers of the sugars in which $—OCH_3$ is substituted for OH and differ from the methylpentoses in which CH_3 replaces one $—CH_2·OH$ grouping. Following a suggestion of Votoček they are more correctly termed methyloglucoses instead of the customary methylglucose. They have become of the greatest importance as affording a means of determining the constitutional formulæ of the di- and poly-saccharides particularly, as it has been generally considered that no stereochemical changes took place during methylation. It is true Hudson has not accepted this conclusion, but his arguments have in the main been countered by Haworth. The latest work does, however, indicate that in certain cases, particularly with furanose derivatives, a change of ring structure is not excluded, so that conclusions based on methylation must not be accepted without caution.

Two methods are available, exhaustive treatment with methyl iodide and silver oxide (Purdie and Irvine, J.C.S. 1903, **83**, 1021; 1904, **85**, 1049), or with methyl sulphate in sodium hydroxide solution (Haworth, J.C.S. 1915, **107**, 8). The former treatment is applied to the methylglucosides or to other derivatives in which the aldehyde group is protected from the oxidising action of the silver oxide. Many of the methyloglucoses are crystalline or form crystalline methylglucosides, others are only known as syrups; they are purified by fractional distillation at low pressures. Only the glucosidic $—OCH_3$ is removed by acid hydrolysis, the remaining four methoxyl groups being stable towards acid.

2:3:4:6-*Tetramethyloglucose* is obtained on complete methylation of α- or β-methylglucoside and hydrolysis of the isomeric pentamethylglucose into which it is converted on etherification by Fischer's method. Tetramethyloglucose is not fermentable.

The isomeric 2:3:5:6-*tetramethyloglucose* is obtained in the form of a syrup on methylating γ-methylglucoside or glucosemonoacetone and subsequent hydrolysis (Irvine, Fyfe, and Hogg, J.C.S. 1915, **107**, 524; Micheel and Hess, Annalen, 1926, **450**, 21); the methylated derivative of the isomeric aldehydo-form, namely, 2:3:4:5:6-*pentamethyloglucose*, being prepared by exhaustive methylation of diethylmercaptoglucose (Levene and Meyer, J. Biol. Chem. 1926, **69**, 175).

The most interesting of all the methyloglucoses is the crystalline 2:3:6 *trimethyloderivative*

CH₂(OMe)CH CH(OH)CH(OMe)CH(OMe)CH OH

This was first isolated from methylated cellulose and subsequently from other methylated polysaccharides, *e g* glycogen, starch, cellobiose, maltose, and lactose (Denham and Woodhouse, J.C.S. *1914, 105, 2357 ; 1917, 111, 244), and has* been fully studied by Irvine and Hirst (J.C.S. 1923, 123, 518).

It is important, as pointed out by Irvine and Black (J C S. 1926, 862), that it can also exist in an unstable furanoid form

CH₂(OMe)CH(OH)CH CH(OMe)CH(OMe)CH OH

which has only a transient existence until it passes into the stable form. The stable form has been obtained by Irvine and McGlynn (J Amer. Chem. Soc. 1932, 54, 356) from both trimethyl γ-methyl and -α-methyl glucosides on hydrolysis, and, as is emphasised by them, this fact makes it impossible to say with certainty that its production from a methylated polysaccharide or disaccharide indicates the presence of a glucose-4-glucoside rather than of a glucose-5 glucoside. This ambiguity has a bearing on the constitution of the disaccharides.

A second reference compound of importance is 2.3:4-*trimethylogIucose* 1:5:

$CH_2(OH)CH\,[CH(OMe)]_3\,CH\,OH$

which is obtained on hydrolysis of fully methylated gentiobiose, melibiose, raffinose, and β glucosan, and indicates that the attachment in these compounds of the two sugar residues is through group 6. This compound is only known as a syrup, but its crystalline methyl glucoside is used for its identification.

An isomeric *3:5.6-trimethyloglucose-1:4* is known .

$CH_2(OMe)CH(OMe)CH\,CH(OMe)CH(OH)CH\,OH$

obtained from glucose monoacetone.

The di- and mono-methyloglucoses are of less interest—they are included in the following table of physical properties ; many of them exhibit mutarotation.

METHYLOETHERS OF GLUCOSE.

	Melting-point	Rotation Initial	Rotation Final
2-methyloglucose	156°–157°	+132°	—
3-methyloglucose	160°	+107°	68°
4-methyloglucose	Syrup	—	52°
5 methyloglucose	Syrup	+80°	60°
6-methyloglucose	143°	+101°	66°
2.3-dimethyloglucose (α)	85°	+82°	48°
,, (β)	108°	+6°	49°
2:3:4 trimethyloglucose 1:5	*Syrup*	+70°	—
2.3:6-trimethyloglucose 1 5	122°	+69°	—
3:5:6 trimethyloglucose 1 4	Syrup	—	—
2:3:4:6-tetramethyloglucose (α) 1 5	103°	+114°	85°
,, (β) 1 5	50°	+73°	85°
2:3.5 6 tetramethyloglucose 1.4	Syrup	−27°	—
2:3:4:6-tetramethylo α-methylglucoside	148°–150°	+151°	—
2.3.4:6 tetramethylo-β methylglucoside	40°–41°	−17°	—
2:3:5.6 tetramethylo α-methylglucoside	Syrup	+104°	—
2:3 5:6 tetramethylo-β methylglucoside	,,	−64°	—
2:3:4.5.6 pentamethyloglucose	,,	−35°	—

The authorities are doubtful as to the structure of the various monomethyl derivatives. A summary of the pertinent literature is given in Chem. Soc. Annual Report, 1934, 165.

Hydrazones.—The hydrazones still continue to be the most useful means of characterising a sugar. A complete list of them is given by Vogel and Georg in "Tabellen der Zucker und ihrer Derivate," Berlin, 1931.

According to Votoček and Valentin (Arh. Hemiju, 1931, 5, 155 ; 1931, A. 1274) the sugar of which a given hydrazone is a derivative can be identified by distilling with 12% HCl. The production of furfuraldehyde indicates a pentose, and of methyl-furfuraldehyde a methylpentose, whilst neither aldehyde is evolved by hexoses.

Reaction with Phenylhydrazine—The behaviour of the carbohydrates with phenylhydrazine is particularly characteristic, and it has further an historical interest, as phenylhydrazine, in the hands of Fischer, served as one of the chief aids in the elucidation of the relationships of members of the group.

Glucose reacts with the reagent in acetic acid solution in two stages. In the cold a phenylhydrazone is formed :

$$C_6H_{12}O_6 + C_6H_5{\cdot}NH\,NH_2 = C_6H_{12}O_5{\cdot}CH{:}N{\cdot}NH\,C_6H_5 + H_2O$$

This is a colourless substance, soluble in water, and is obtained in two *modifications*, one or the other predominating according to the method of preparation. Similar compounds,

with asymmetrically disubstituted hydrazines—for example, benzylphenylhydrazine—are often less soluble and more characteristic. Mannose is remarkable in forming an almost insoluble phenylhydrazone. The hydrazones of lactose and maltose are very soluble.

At the temperature of boiling water, glucose reacts with excess of phenylhydrazine to form the phenylosazone

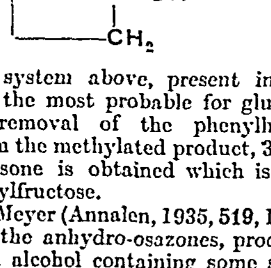
$$CH_2(OH)\cdot[CH(OH)]_3\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$$

For obtaining a maximum yield of glucosazone by Fischer's method the ratio of phenylhydrazine hydrochloride and crystallised sodium acetate should be 1 : 2·7. The yield increases with the amount of the reagents up to 3·2 g. of phenyl-hydrazine in 20 c.c. of water per g. of glucose. The reaction is not completed within less than 3 hours, but beyond this there is decomposition (Taketomi and Miura, J. Soc. Chem. Ind. Japan, 1929, 32, 776).

The yellow osazone is filtered and carefully washed; it may be crystallised from most organic solvents, the most suitable being a dilute solution of pyridine. Glucose, mannose and fructose form the same phenylosazone, as they differ only in the relative positions of groups which are destroyed in the formation of the osazone.

Too much reliance must not be placed on the melting-points of the osazones in identifying unknown sugars in solution, as these depend very largely on the method of purification adopted and on the rate of heating. Disubstituted hydrazines do not directly form osazones with glucose, though these may be prepared from the osones.

Evidence is now forthcoming from a study of the methylation products of glucosazone that the osazones possess a ring structure (E. E. Percival and E. G. V. Percival, J.C.S. 1935, 1398; *see also* Engels, J. Amer. Chem. Soc. 1935, 57, 2419).



The ring system above, present in fructopyranose, is the most probable for glucosazone since, on removal of the phenylhydrazine residues from the methylated product, 3:4:5-trimethylglucosone is obtained which is reduced to a trimethylfructose.

Diels and Meyer (Annalen, 1935, 519, 157) have found that the anhydro-osazones, produced by boiling with alcohol containing some sulphuric acid, have well defined melting-points and are very suitable for identification purposes.

Votoček (Bull. Soc. chim. 1926, [iv], 39, 278) has described the 2:4-dibromophenyl- and the three iodophenyl-hydrazones and -osazones of the sugars. The iodophenylosazones are of no value analytically, but the 2:4-dibromophenylhydrazone furnishes a means of quantitative separation of galactose from all the more common sugars except arabinose.

Diphenylmethanedimethyldihydrazine,

$$CH_2(C_6H_4\cdot NMe\cdot NH_2)_2,$$

(J. von Braun and Bayer, Ber. 1925, 58, [B], 2215) does not react with ketoses, and only with aldoses *in which at least two of the three* —CH·OH groups following the —CHO group have the same spatial arrangements. It is thus useful in isolating mannose. Methylphenylhydrazine, which reacts more rapidly with ketoses than with aldoses, may be used to distinguish fructose from glucose.

To recover the original sugar from the phenylhydrazone, it is boiled in water with a slight excess of benzaldehyde. The phenylhydrazine is removed as benzaldehyde phenylhydrazone, the excess of aldehyde extracted by ether, and the sugar solution concentrated *in vacuo.*

p-Nitrobenzaldehyde can conveniently be substituted for benzaldehyde in the regeneration of sugars from their hydrazones in view of the greater insolubility of its hydrazone. With the disubstituted hydrazones better results are obtained by using formaldehyde.

The phenylhydrazine residues may be removed from the osazones by heating with fuming hydrochloric acid. Compounds termed osones are formed:

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot CO\cdot CHO$$

These are colourless syrups; they act as strong reducing agents, combine directly with phenylhydrazine, and are non-fermentable. The slightly soluble osazones of the disaccharides, and of the pentoses, are converted into osones on boiling with benzaldehyde.

When reduced by means of sodium amalgam, the osones are converted into ketoses, and not into the aldoses from which they were formed. Thus it is possible to pass from glucose to fructose—a transformation of great importance —the stages being:

glucose → phenylosazone → osone → fructose

Another important transformation is that from glucose to mannose, which is based on the fact that gluconic acid (*v. supra*), when heated with quinoline, is converted into a mixture of gluconic and mannonic acids. The stages in this case are:

$$\text{glucose} \xrightarrow{\text{oxidation}} \left\{\begin{matrix}\text{gluconic}\\ \text{acid}\end{matrix}\right\} \rightarrow \left\{\begin{matrix}\text{mannonic}\\ \text{acid}\end{matrix}\right\} \xrightarrow{\text{reduction}} \text{mannose}$$

By the aid of these two reactions Fischer was able to pass from the synthetical α-acrose to *d*-glucose, *d*-fructose, and *d*-mannose, and so effect the complete synthesis of the naturally occurring hexoses.

Cyanohydrin Synthesis.—*The aldoses combine* directly with hydrogen cyanide, forming nitriles, which, when hydrolysed, give rise to acids containing one carbon atom more than the original carbohydrate. The lactones of these acids, when reduced with sodium amalgam, yield

the corresponding aldoses with one carbon atom more than the original carbohydrate :

$$C_5H_{11}O_5 \, CHO + HCN = C_5H_{11}O_5 \, CH(OH) \, CN \rightarrow C_5H_{11}O_5{\cdot}CH(OH)CO_2H \rightarrow C_5H_{11}O_5{\cdot}CH(OH)CHO$$

In this manner arabinose is converted into glucose, glucose into glucoheptose. Fischer has continued the process as far as the aldononose.

Actually two isomerides are formed at each stage, and arabinose gives both glucose and mannose.

Degradation.—The converse change from *glucose to arabinose has been effected* by several different methods.

Wohl (Ber. 1893, 26, 730, etc.) heated glucose oxime with concentrated sodium hydroxide, so converting it into gluconic acid nitrile, from which, on further heating, hydrogen cyanide was eliminated and *d*-arabinose formed:

$$C_5H_{11}O_5{\cdot}CHO \rightarrow C_5H_{11}O_5{\cdot}CH{:}N\,OH \rightarrow C_5H_{11}O_5{\cdot}CN \rightarrow C_5H_{10}O_5$$

In practice the method adopted is to heat the oxime with acetic anhydride and a trace of zinc chloride ; a vigorous reaction ensues, and the pentacetate of gluconic acid nitrile is formed, from which hydrogen cyanide is eliminated by treatment with ammoniacal silver oxide.

Ruff (Ber. 1898, 31, 1573) oxidises the calcium salt of gluconic acid with hydrogen peroxide in presence of a ferrous salt (Fenton's *method). The carboxyl group is eliminated* and arabinose formed.

Neuberg (Biochem. Z. 1908, 7, 527) effects the elimination of the elements of formic acid from gluconic and similar acids by electrolysis.

Weerman (1915, A, 387) obtains gluconamide by saturating gluconolactone in alcoholic solution with ammonia. On subsequent treatment with hypochlorous acid the amide is decomposed according to the scheme

$$R\,CH(OH)\,CO\,NH_2 \rightarrow R{\cdot}CH(OH){\cdot}N{\cdot}C{:}O \rightarrow R{\cdot}CHO$$

According to Irvine the reactions proceed with the utmost smoothness and constitute a great improvement on the methods hitherto in use. The reaction has been applied to glucose, galactose, *l*-mannose, and *l*-arabinose.

Desmutation Products of the Sugars.

These include unsaturated substances in which a double bond has been introduced into the carbon chain, as well as inner anhydrides, and are of interest both on account of the insight they afford into the structure of the complex glucose molecule, and as giving starting materials for new syntheses. The first changes in glucose under the influence of alkalis, of ferments, and of bacteria, are still only partially understood, whilst the presence of the deoxy sugars in plants and animals adds new interest to the partially reduced glucoses.

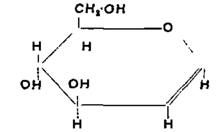
The unsaturated compounds are :

Glucal	with double-bond joining carbons	1 and 2
*iso*Glucal	,, ,, ,,	2 and 3
Glucoseen -5:6	,, ,, ,,	5 and 6
Glucoseen -1:2	,, ,, ,,	1 and 2

Glucal, $C_6H_{10}O_4$. — When acetobromo glucose is reduced by zinc dust and acetic acid triacetylglucal is formed with a double bond between carbons 1 and 2 (Fischer, Ber. 1914, 47, 196 ; Fischer, Bergmann, and Schotte, *ibid.* 1920, 53, [B], 509). The pyranose structure assigned to glucal:

$$HO{\cdot}CH_2{\cdot}\underbrace{CH{\cdot}CH(OH)CH(OH)CH{:}CH}_{O}$$

or



has received independent confirmation by *Hirst and Woolvin (J.C.S. 1931, 1131). The* fact has significance owing to the easy conversion of glucal into α-methylmannoside (Bergmann and Schotte, Ber. 1921, 54, [B] 1564) by means of perbenzoic acid. Strong evidence is thus afforded for the pyranose structure of mannose contrary to the view of Hudson (J. Amer. Chem. Soc. 1930, 52, 1680). Similar glucals are obtained from the other sugars. Their reaction with perbenzoic acid is being studied by Levene and Tipson (J. Biol. Chem 1931, 93, 631), who predict their use for preparing and interconverting some of the rarer sugars. Whilst glucal in *this reaction yields* mannose, 3-methylglucal yields 3-methylglucose (Levene and Raymond, *ibid.* 1930, 88, 513), and the 4-galactosidomannose from lactal is a mixture of two sugars (Watters and Hudson, J. Amer. Chem. Soc. 1930, 52, 3472).

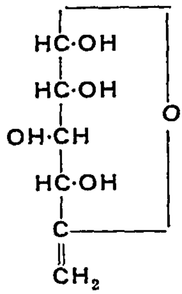
On treatment with dilute sulphuric acid in the cold glucal is converted into deoxyglucose (Bergmann, Schotte, and Lechinsky, Ber. 1922, 55, [B], 158). The method is a general one and has been used for the synthesis of the deoxypentoses.

*iso***Glucal.**—When glucal triacetate is boiled with water the double bond moves along the chain to form the diacetate of *iso*glucal (Bergmann and Freudenberg, Ber. 1931, 64, [B], 158 ; Annalen, 1929, 470, 51):

$$HO{\cdot}CH_2\,\underbrace{CH\,CH(OH)CH{:}CH\,CH}_{O}\,OH$$

On reduction a bisdeoxyglucose is formed.

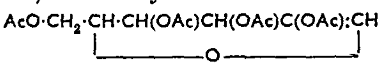
Glucoseen-5.6 is an unsaturated anhydroglucose which has lost a molecule of water between carbons 5 and 6 leaving the side chain attached by a double bond. α-Tetra-acetyl-*d* glucoseen has m.p. 115°, $[\alpha]_D$ +110 9° ; the β-isomeride has m.p. 119°, $[\alpha]_D$ −35°. The corresponding β-methyl *d*-glucoseenide, m p. 109°–110°, $[\alpha]_D$ 115 5°, is very sensitive to acids (Helferich and Himmen, Ber. 1928, 61, [B], 1825, *see also* Maurer, Ber. 1929, 62, [B], 332).



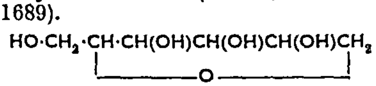
Solutions of the hydrolysed glucoseenide give with phloroglucinol and many other reagents colorations closely resembling those of certain components of wood or of lignin itself.

Unsaturated substances are present in wood and it is quite possible that glucoseen is related to the transition products between glucose and lignin.

Glucoseen-1:2 is obtained under somewhat special conditions from acetobromoglucose by the action of diethylamine (Maurer, Ber. 1929, 62, [B], 332). It is only known as its tetra-acetate

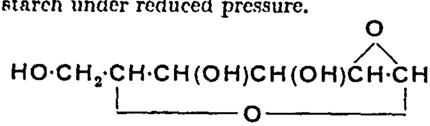


On reduction and hydrolysis of this compound a substance identical with styracitol, which occurs naturally, is obtained, proving styracitol to be 1:5-anhydro-*d*-sorbitol (Zervas, Ber. 1930, 63, [B], 1689).

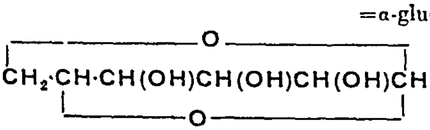


Glucosans.—Crystalline anhydrides of the sugars exist having a second oxygen ring in addition to the 1:5 oxygen bridge. These are termed glucosans.

α-Glucosan, discovered by Gélis (Compt. rend. 1860, 51, 331), is prepared by Pictet by heating α-glucose in a vacuum. The hydroxyls on carbons 1 and 2 are on the same side of the plane of carbons, and it is here that water is eliminated, forming a 1:2-oxygen bridge (Pictet, Compt. rend. 1920, 171, 243). From β-glucose, where the hydroxyl on carbon 1 is on the other side of the plane of the ring, no such elimination is possible, but it takes place with the adjacent side chain hydroxyl, forming a 1:6-oxygen bridge. This is termed β- or lævoglucosan (Pictet, Helv. Chim. Acta, 1918, 1, 87; 1920, 3, 640); it is prepared by distilling cellulose or starch under reduced pressure.



=α-glucosan

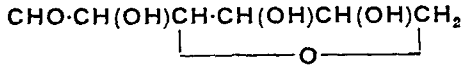


=β-glucosan

	M.p.	$[\alpha]_D$
α-glucosan	108°	+69·8°
β-glucosan	179°	−66·2°

A form of glucose anhydride was once suggested as the unit of the polysaccharides. A simple methylated glucose anhydride—1:4—has been prepared by Hess (Ber. 1927, 60, [B], 1898) from the actual 2:3:6-trimethylglucose which is obtained from methylated starch, glycogen, and cellulose on complete hydrolysis. This anhydride, however, has none of the properties of a methylated saccharide.

Another anhydroglucose is the 3:6-anhydride of Fischer and Zach (Ber. 1912, 45, 456, 2068):



which is regarded as an aldehyde since it gives a positive test with Schiff's reagent. It can be prepared from glucose monoacetone (*cf.* Ohle, Ber. 1928, 61, [B], 1211; Freudenberg, *ibid.* 1750; also *ibid.* 1208, 1870).

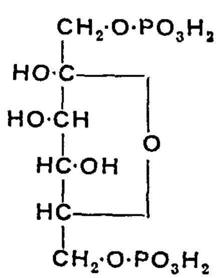
A 2:5-anhydroglucose or *epichitose* is obtained by the action of nitrous acid on epichitosamine.

Polymers of Glucosan.—When β-glucosan is heated with zinc dust at 250°/15 mm. in an atmosphere of hydrogen (Irvine and Oldham, J.C.S. 1925, 127, 2903) it polymerises to compounds of the nature of synthetic dextrins, which have been separated into fractions by the addition of alcohol to the aqueous solutions. With the exception of pentaglucosan a series of polyglucosans from mono- to octaglucosan has been described. It is supposed that glucosan is first converted into glucose, one molecule of which condenses with a second molecule of glucosan, and the process continues catalytically. Triglucosan is regarded as glucosan maltoside. The behaviour of these compounds towards emulsin and amylase is described by Pictet (Castan and Pictet, Helv. Chim. Acta, 1925, 8, 946; Pictet and Salzmann, *ibid.* 948). Emulsin forms glucose and dihexosan from trihexosan, maltose from hexahexosan.

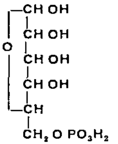
Phosphoric Esters.

The greatest importance now attaches to these derivatives of glucose as essential mutation products during alcoholic fermentation, and certain vital processes in the body, including that of bone formation.

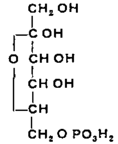
Hexose diphosphate formed during the first stage of fermentation is formulated as the 1:6-diphosphoric ester of fructofuranose:



The two monophosphates have been shown to be glucopyranose-6-phosphoric ester (I) and fructofuranose-6-phosphoric ester (II):



I.



II.

Further, when glucose is fermented with dried yeast, trehalose monophosphate is formed (Robison and Morgan, Biochem. J. 1928, 22, 1277, 24, 119)

These hexosephosphates are hydrolysed when *boiled with acids, but the different esters* liberate phosphoric acid at varying rates. The phosphatases which hydrolyse them are very widely distributed.

The synthetic phosphoric esters have been prepared by the action of phosphorus oxychloride on the sugars in presence of calcium carbonate. Neuberg (Biochem Z 1910, 23, 515; 26, 514, 1911, 36, 5) describes monophosphates of glucose and galactose · in these the acid residue is considered to be attached to carbon 1. Neither is fermented by yeast.

The Carbohydrate Alcohols.

These alcohols are widely distributed in the vegetable kingdom, where they occur, as a rule, uncombined with other substances. As a class they are readily soluble in water, crystallise well, and have a small rotatory power On cautious oxidation they give in turn a reducing sugar, monobasic acid, and dibasic acid. They are obtained by reduction of the corresponding aldose or ketose carbohydrates with sodium amalgam, but, as a rule, owing to transformations in the alkaline solution, a mixture of *alcohols is produced* They are not fermentable by yeast though attacked by a variety of bacteria and moulds. They do not reduce Fehling's solution

The wider distribution of these alcohols is continually being noted, particularly that of the rarer varieties. At one time mannitol was the only representative of the alcohols known to occur in the algæ, but recently Haas has detected both dulcitol and sorbitol in a red seaweed The occurrence of these two sugar alcohols in the same plant is noteworthy, for hitherto sorbitol has practically only been found in the Rosaceæ.

The alcohols corresponding to the synthetic sugars are known. Those which occur naturally are:

Erythritol, $C_4H_{10}O_4$, present in a number of lichens, crystallises in large transparent prisms, m p. 126°. Being the *meso*form it is *optically inactive. The synthetic optically* active varieties have $[\alpha]_D$ ±4·4°.

Adonitol, $C_5H_{12}O_5$, the only naturally occurring pentose alcohol, corresponds to ribose. It is found in *Adonis vernalis*. It crystallises in prisms, m.p. 102°, is optically inactive, and has a sweet taste.

***d*-Mannitol**, $C_6H_{14}O_6$, the alcohol corresponding to mannose, is widely distributed

It crystallises in colourless rhombic prisms, m p. 166°. It is optically inactive, but on the addition of borax it becomes strongly dextrorotatory, a mixture containing 10% mannitol and 8% borax having $[\alpha]_D$ +22 5°. This mixture is strongly acid. With caustic soda and other alkalis it becomes lævo-rotatory.

Mannitol has a slightly sweet taste, is not fermentable by yeast, sorbose bacteria oxidise it to fructose, and it is attacked by many other races *It does not reduce Fehling's solution*, or interact with phenylhydrazine. It is easily oxidised.

Polygalitol (Shinoda and Sato, Ber. 1932, 65, [B], 1219) is 1.5-anhydromannitol, m p. 142°–143°, $[\alpha]_D^{16}$+47 81°.

***d*-Sorbitol**, $C_6H_{14}O_6$, the alcohol corresponding to glucose, *was discovered in mountain*-ash berries by Boussingault and is found in the fruits of many of the Rosaceæ.

Sorbitol crystallises with 1 mol H_2O in slender needles, m.p. 55°. The anhydride has m p 110° It is very soluble in water, sparingly so in alcohol It has $[\alpha]_D$ −1·73°, which becomes +1 4° in presence of borax. It is faintly sweet, non fermentable, but is oxidised by *B xylinum* to sorbose

d *Sorbitol* is marketed as a substitute for sugar under the name of *Sionin*; it appears that in limited quantity it can be tolerated in illness (Chem and Ind 1929, 48, 573).

Styracitol is 1·5-anhydrosorbitol and has been synthesised by the reduction of tetra acetyl hydroxyglucal (Zervas, Ber. 1930, 63, [B], 1689) The occurrence of the 1·5 ring in the alcohols is of interest; it indicates an intermediate stage *in the biological reduction of* aldose to alcohol It has m p. 157° and $[\alpha]_D^{17}$ −49 4° in water.

Dulcitol, $C_6H_{14}O_6$, the alcohol from galactose, is also of wide occurrence. It has m p 188° and is optically inactive.

***d* Iditol** is found in mountain ash berries but *is probably of secondary* origin (Bertrand, Bull Soc. chim. 1906, [iii], 33, 166). It has m p 73° and $[\alpha]_D$ −3 50° in water.

Perseitol, $C_7H_{16}O_7$, a heptose alcohol identical with *d*-mannoheptitol, is obtained from the seeds of species of *Persea*. It crystallises in needles, m p. 188°, $[\alpha]_D$ −1·3° becoming $[\alpha]_D$ +4 5° in borax solution.

Volemitol, $C_7H_{16}O_7$, obtained from *Lactarius volemus*, is identical with α sedoheptitol. It forms slender needles, m p. 153°, $[\alpha]_D$ +2 2°.

The Carbohydrate Acids.

These are acids containing the same number of carbon atoms as the aldose carbohydrates from which they are derived. They are either mono or di-basic. Ketoses on oxidation yield acids with fewer carbon atoms than the original carbohydrate.

The monobasic acids are formed on oxidising the aldehyde group to carboxyl, generally by means of bromine or dilute nitric acid. More energetic oxidation converts also the primary alcohol ($-CH_2\cdot OH$) group into acid (CO_2H)

Glucuronic acid, which is of considerable importance physiologically, is a type of monobasic

acid, in which the aldehyde group is intact, and the primary alcohol group oxidised to carboxyl.

The monobasic acids are transformed in aqueous solution, particularly on evaporation on the water-bath, into lactones which crystallise well. The dibasic acids similarly sometimes form double lactones.

The most important property of gluconic and isomeric acids is their behaviour on heating with pyridine or quinoline, when they are transformed into isomerides, rearrangements of the groups attached to the α-carbon atom taking place. Thus, when gluconic acid is heated with quinoline or pyridine at 130°–150°, it is partially converted into mannonic acid. This behaviour has been of the utmost importance in effecting the synthesis of the carbohydrates.

Gluconic Acid, $C_6H_{12}O_7$, always contains a proportion of lactone. It is slightly lævo-rotatory at the instant of solution, but becomes dextro-rotatory as the transformation to lactone takes place, the final figure for a mixture in equilibrium of acid and lactone being about +19°. The lactone crystallises in slender needles, m.p. 130°–135°. It has $[\alpha]_D$ +68° when first dissolved, falling to +19° for the solution in equilibrium with the acid.

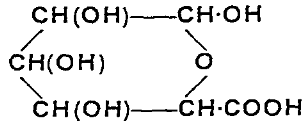
A number of commercial uses for gluconic acid have now been found, and practical methods for its preparation worked out.

Calcium gluconate, being soluble, practically tasteless, and non-irritating to tissues, is being increasingly used in medicine; it may be administered by the mouth or by subcutaneous injection. Its use for the medical treatment of calcium deficiency is arousing interest. The property of the lactone of slowly regenerating acid when dissolved in water is being utilised in several directions, especially as it can be controlled within certain limits by varying the temperature and concentration. The lactones further have a slightly sweet and not an acid taste. Thus they may with advantage replace fruit acids in the manufacture of powders to be used for the preparation of fruit jellies, and in baking powders. In the former case the lactones may be dissolved simultaneously with sugar and pectin to a clear solution which will jell on boiling. In the latter the evolution of carbonic acid from lactone is more gradual and the leavening action more uniform. The gluconates are useful in the preparation of homogeneous pastes such as dentifrices and for polishing. The aluminium salt and the acid have potentialities in tanning.

The acid is manufactured from glucose by fermentation, by chemical oxidation, or by electrolytic oxidation in the presence of a small quantity of a bromide. The last method described by Isbell and Frush (Bur. Stand. J. Res. 1931, 6, 1145) gives nearly quantitative yields and appears economical.

Increased yields are obtained when the oxidation with aqueous bromine is conducted in presence of calcium or barium benzoate to remove the hydrogen bromide from the system (Hudson and Isbell, J. Amer. Chem. Soc. 1929, 51, 2225).

Uronic Acids.—The general term "uronic acid," first suggested by Schryver, is applied to those sugar derivatives in which the primary alcohol or side chain carbon group is oxidised to carboxyl:



Glucuronic and galacturonic acids are widely distributed in plants and mannuronic acid is present in seaweeds and in hemicelluloses. Polyuronic acids are also widely distributed.

They are readily prepared from any polysaccharide or suitable glycoside (glucoside) in which the reducing group is protected and the side chain group is free, by oxidation with bromine in neutral or alkaline solution. In this way glucuronic acid is obtained from sucrose (Nanji, Paton, and Ling, J.S.C.I. 1925, 44, 253T), whilst milk sugar gives galacturonic acid.

Similarly by oxidation of the α- and β-methyl glucosides with bromine in pyridine solution the corresponding α- and β-methyl-glucuronic acids are formed (Bergmann and Wolff, Ber. 1923, 56, 1060).

The uronic acids can be quantitatively estimated by heating with hydrochloric acid when they are converted to carbon dioxide and furfural (*see* Nanji, etc., *l.c.*).

Glucuronic Acid is conveniently prepared from gum arabic, about 50 g. being obtained from 1 kg. of gum (Weinmann, Ber. 1929, 62, [B], 1637). It has m.p. 154°, $[\alpha]_D$ +36·2°, and exists in two modifications. The initial rotation is +3·6°. The corresponding lactone formed in boiling aqueous solutions crystallises well, m.p. 175°–178°, $[\alpha]_D$ +192°. The characteristic compound with p-bromophenylhydrazine (Neuberg, Ber. 1899, 32, 2386, 2395) has m.p. 236°.

A long list of the paired glucuronic acids separated in the urine after administration of various organic compounds is given by Neuberg in Oppenheimer's "Handbuch der Biochemie," 1924, I, 356.

Galacturonic Acid, m.p. 159°, $[\alpha]_D$ +55·6°, is conveniently made from commercial lemon pectin (Link and Dickson, J. Biol. Chem. 1930, 86, 491). Ehrlich and Schubert have prepared it in α- and β-forms from sugar beet (Ber. 1929, 62, 1974). The α-form crystallised from hot aqueous solution has physical constants similar to the above, $[\alpha]_D$ originally being +107°. The β- variety is obtained on boiling the α-form with a large excess of absolute alcohol and rapid evaporation of the solvent. It has m.p. 160°, $[\alpha]_D$ +27°, rising to +55·3°. According to their colour reactions the α-form has an aldehydic and the β-form a pyran ring structure. The semicarbazone (Kiliani, Ber. 1923, 56, [B], 2016) has m.p. 190°.

dl-Galacturonic acid is obtained by reduction of mucic acid with sodium amalgam (Niemann and Link, J. Biol. Chem. 1932, 96, 449).

Mannuronic Acid (Kiliani, Ber. 1922, 55, [B], 87; 1923, *l.c.*) forms a lactone, m.p. 205°–206°, $[\alpha]_D$ −196°, and a semicarbazone, m.p. 189°.

Physiologically the uronic acids are among the most important oxidation products of the

sugars ; they are apparently a means which the organism uses to protect itself against toxic agents.

A number of polyuronic acids are now being identified, and there is little doubt that they are of wide occurrence. Thus *d*-mannuronic acid is present in the alginic acid of seaweeds (Nelson and Cretcher, J. Amer. Chem Soc. 1929, 51, 1914), and probably in the hemicellulose of *white oak*. *Apple pectin contains digalacturonic* acid, whilst arabinogalacturonic acid is present in orange pectin (Bowmann and McKinnis, *ibid.* 1930, 52, 1209). *l* Rhamnose-*d* galacturonic complexes have been found in Cholla gum (Sands and Klaas, *ibid.* 1929, 51, 3441) and in flax seed mucilage (Anderson and Crowder, *ibid* 1930, 52, 3711)

Saccharic Acid, $C_6H_{10}O_8$, is obtained on oxidising glucose and all carbohydrates which contain glucose, also from sorbitol, gluconic acid, and glucuronic acid.

Saccharic acid is a syrup, $[\alpha]_D$ $+8°$, increasing to $+22\ 5°$ It forms a characteristic mono potassium salt $C_6H_9O_8K$ The lactone $C_6H_8O_7$ has m.p 130°–131°, $[\alpha]_D$ $+37\ 9°$, decreasing to $2\ 25°$ for the equilibrium mixture with the acid.

Mucic Acid is obtained from galactose, lactose, raffinose, dulcitol, and all carbohydrates which contain galactose. It is a microcrystalline powder, m.p. 213°–214° It is optically inactive and cannot be resolved into optically active isomerides.

Disaccharides.

The formulæ of the disaccharides have undergone revision on the basis of the accepted pyranose formula for glucose ; only in sucrose is the furanose form present. By a variety of methods the carbon concerned in the attachment of the second monosaccharide has been determined to be either 4 or 6. The following table indicates the best known disaccharides:

Type I.	With reducing properties	Final Rotation $[\alpha]_D$
Maltose	$=\beta$ glucose-4-α-glucoside	$+136°$
Cellobiose	$=\beta$ glucose-4-β glucoside	$+35°$
Lactose	$=\alpha$ glucose 4 β galactoside	$+55\ 3°$
Gentiobiose	$=\beta$ glucose-6-β glucoside	$+9\ 6°$
Melibiose	$=\beta$ glucose-6 α galactoside	$+143°$
Turanose	$=\beta$-fructofuranose - 6 - α - glucoside	$+75\ 3°$
Primeverose	$=\alpha$-glucose 6 β-*d*-xyloside	$-3\ 4°$
Vicianose	=glucose 6-β-*l*-arabinoside	$+39\ 7°$
Rutinose	=glucose rhamnoside	$+3\ 2°$
Type II	**No reducing properties**	
Sucrose	$=\alpha$ glucopyranose - fructo furanose	$+66\ 37°$
Trehalose	$=\alpha\alpha$ diglucopyranose	$+197°$
*iso*Trehalose	$=\beta\beta$-diglucopyranose	$-39°$
*neo*Trehalose	$=\alpha\beta$ diglucopyranose	$+100°$
glucoxylose	=glucose-xylose	$-36\ 5°$

The disaccharides when fully methylated form octamethyl derivatives which, when hydrolysed by acids, break down into a tetramethyl derivative of that hexose, which functioned as the glycoside, and a trimethyl derivative of the other hexose.

Maltose, cellobiose, and lactose form 2.3 6 trimethylglucose-1:5, whereas gentiobiose and melibiose give rise to 2 3.4 trimethylglucose 1.5. The former compound has a free hydroxyl at carbon 4 and the latter at carbon 6, indicating that these positions are concerned in the attachment to the other hexose molecule.

Confirmatory evidence is afforded by oxidising maltose to maltobionic acid, introducing nine methyl groups and hydrolysing with acids, when in addition to 2:3.4:6 tetramethyl glucose the second product obtained is 2:3:5.6-tetramethyl γ-gluconolactone with a potentially free hydroxyl group at carbon 4. When the same method is applied to melibiose the product is 2 3 4.5-tetramethylgluconic acid with a free hydroxyl at carbon 6.

Yet a third proof has been afforded by the gradual degradation of maltose through its oxime to glucoarabinose and glucoerythrose, which last is incapable of forming an osazone.

The fourth hydroxyl group of glucose is not characterised by particular activity, and its preferential use in the formation of natural polysaccharides is due to some mechanism more selective than simple etherification.

Maltose, $C_{12}H_{22}O_{11}$, is β-glucose-4-α-glucoside and is therefore a reducing disaccharide. It was perhaps obtained from starch by De Saussure in 1819, and was prepared by Varry, who failed to recognise it as a distinct substance. Dubrunfaut, in 1847, further examined it and gave the name maltose, but regarded it as a trisaccharide. O'Sullivan showed, in 1872, that it is a disaccharide, and gave a fuller description of its characters.

Maltose is primarily a hydrolytic product of starch, and its occurrence in nature is mainly under conditions where it has been derived from this reserve material. Thus it is found in the leaves of plants, in germinating seeds, and in malt. Maltose has been reported to have been found in the free state in the tubercles of *Umbilicus pendulinus* (Bridel, Bull. Soc. Chim. biol 1925, 7, 181) and in the rhizomes of *Mercurialis perennis* (Gillot, J. Pharm. Chim. 1923, [vii], 28, 148; 1925, [viii], 1, 205), where the amount increases during the summer months to a maximum of about 2% in September. It is said to be formed in sweet potatoes on cooking (Gore, Ind. Eng. Chem. 1923, 15, 938). Under abnormal conditions it is found in the urine. It is a constituent of commercial glucose.

Starch is converted by the enzyme diastase first into dextrins and then into maltose, which is also obtained when starch is hydrolysed by acids. Diastase also acts on glycogen, forming maltose amongst other products.

Maltose is always prepared by the action of diastase, usually malt extract, on starch paste ; its purification from the dextrins present, which are soluble in alcohol, is often a matter of difficulty. Baker and Day (Brit. Assoc. Report, Dublin, 1908, 671) recommend the use of diastase of ungerminated barley, which converts starch into maltose, about 60%, and a amylodextrin which can easily be separated by one precipitation with alcohol.

Maltose shows many of the properties of glucose and forms two series of derivatives. The α-form has $[\alpha]_D$ +168°, the β-form, which is the normal, has +118° and the equilibrated mixture +136°. According to v. Euler and Helleberg (Z. physiol. Chem. 1924, **139**, 24) the maltose first produced by the enzymic hydrolysis of starch by malt extract is the β-form.

Maltase is the only enzyme able to effect the hydrolysis of maltose. Fermentation by yeasts occurs only after hydrolysis.

The product variously known as *iso*maltose, gallisin, revertose is now regarded as a mixture of maltose with other substances.

Cellobiose is β-glucose-4-β-glucoside, and thus differs from maltose in the same way that β-methylglucoside differs from the α-isomeride. It is a remarkable fact that starch and cellulose which make up so large a proportion of the vegetable kingdom are polymers of such closely related isomerides and yet so very different in appearance, physical properties, and biological function.

Cellobiose is prepared by hydrolysis of the octa-acetate formed by the action of acetic anhydride on filter paper. It is hydrolysed by emulsin, and it has been synthesised. *Cellotriose* and *cellotetrose* are known, also *cellodextrins*, which range in size from chains of 10 to chains of 30 β-glucose units.

Lactose, α-glucose-4-β-galactoside, or **Milk Sugar**, $C_{12}H_{22}O_{11}$, was first separated from whey by Fabriccio Bartoletti in 1619, and termed *nitrum seri lactis*. It is found in the milk of all mammals, human milk contains from 5 to 8% of milk sugar, cow's and ewe's milk from 4½ to 5%, mare's and ass's milk about 6–7%. It has not been found in plants.

It is manufactured by evaporation of whey, purified by recrystallisation, and obtained as a white powder in the α-form $[\alpha]_D$ +90°. The β-form has +35° and the equilibrated mixture +55·3°.

Lactose behaves like glucose giving rise to two series of isomeric derivatives. It is hydrolysed only by lactase, a β-galactosidase found in a few torulæ and some Kephir preparations. It is particularly prone to undergo lactic and butyric acid fermentations.

A *neo*lactose is obtained by a somewhat complex rearrangement when lactose octa-acetate and anhydrous aluminium chloride interact. It proves to be β-*d*-galactosido-*d*-altrose (Kunz and Hudson, J. Amer. Chem. Soc. 1926, **48**, 1978, 2435).

A keto sugar, lactulose (=fructose-4-β-galactoside), is obtained by the action of calcium hydroxide on lactose (Montgomery and Hudson, J. Amer. Chem. Soc. 1930, **52**, 2101).

The synthetic galactosido-glucoside of Fischer and Armstrong obtained as a syrup and at one time considered to be identical with melibiose is regarded by Schlubach and Rauchenberger as lactose (Ber. 1925, **58**, [B], 1184 ; 1926, **59**, [B], 2102).

Gentiobiose is β-glucose-6-β-glucoside. It has been proved to be the sugar of amygdalin, of α-crocin, as well as of the gentian-glucosides, and of certain anthocyanins, and is probably still more widely distributed. It has been synthesised by Helferich and others (Annalen, 1926, **447**, 27). It is obtained by the action of dilute acids or of invertase on the trisaccharide gentianose. It has been synthesised both chemically and by means of enzymes, and is hydrolysed by emulsin.

The anhydrous crystals of the β-form exhibit mutarotation initially, $[\alpha]_D$ −11° becoming $[\alpha]_D$ +9·6°. The α-form has $[\alpha]_D$ +31°.

Melibiose is β-glucose-6-α-galactoside. It was first obtained together with fructose by the partial hydrolysis of raffinose, either by dilute acids or certain bottom fermentation yeasts. The method of preparation has been reviewed by Harding (Sugar, 1923, **25**, 514).

The isomeric α-glucose-6-β-galactoside has been synthesised by Helferich and Rauch (Ber. 1926, **59**, [B], 2655).

It exhibits mutarotation, the α-form having $[\alpha]_D$ +197°, the β-form +125°, and the equilibrium mixture +143°.

It is hydrolysed by an enzyme melibiase which is an α-galactosidase present in bottom fermentation but not in top fermentation yeasts.

Turanose—β-fructofuranose-6-α-glucoside—has a free ketonic group and is the only sugar of the maltose type containing fructose which is present in the pyranose form.

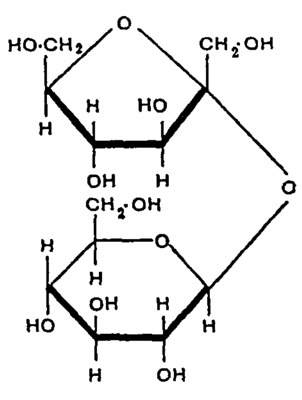
Hudson and Pacsu (J. Amer. Chem. Soc. 1930, **52**, 2519) state that the pure sugar, m.p. 157°C., is non-hygroscopic and mutarotates from $[\alpha]_D$ +22° initially to a final value of +75·3°.

It is hydrolysed fairly rapidly by α-glucosidase but not by invertase, emulsin, or rhamnase (Aagaard, Tids. Kjemi, 1928, **8**, 5, 16, 35).

It is obtained from a trisaccharide (melezitose) on hydrolysis with 20% acetic acid.

Sucrose=α-glucopyranose-fructofuranose.

Great interest still attaches to the formula of sucrose and to the attempts to effect its synthesis. It forms an octamethylo derivative which on hydrolysis yields 2:3:4:6-tetramethylglucopyranose and 1:3:4:6-tetramethylfructofuranose. Haworth accordingly formulates it as :



In contrast to most of the sugars it crystallises exceedingly well ; this is almost certainly due to the fact that one substance only is present in solution, and not a mixture of isomerides. It lacks both aldehydic and ketonic properties, being without action on Fehling's solution.

Pictet and Vogel (Helv. Chim. Acta, 1928, **11**, 901) describe two different forms of sucrose. The A modification, m p. 183°, crystallises from aqueous acetone, pyridine, and several other organic solvents; the B form, m p. 171°, is obtained only from aqueous methyl alcohol. The differences appear to be purely physical and the conversion of B into A is instantaneous in water.

The synthesis of sucrose is still, in the words of Emil Fischer, the unattained goal of sugar chemistry. The first claim by Marchlewski in 1899 has been long since discredited, and the same applies to that of Pictet and Vogel in 1928 (Helv. Chim Acta, 1928, **11**, 436; Ber 1929, **62**, [B], 1418)

The discovery that the form of fructose present in sucrose is the γ or active form, and not the fructopyranose modification, explained the many failures in the past by careful workers to effect the synthesis which resolves itself into the union of normal glucose with γ fructose.

As sucrose is at the same time both an a glucoside and a fructoside it should be capable of being hydrolysed by two enzymes Invertase, which hydrolyses cane sugar, also hydrolyses the labile γ fructosides, and it is considered to contain a fructosidase and not to act on both sugars simultaneously. Willstatter and Bamann (Z. physiol. Chem 1926, **151**, 273) have separated maltase and invertase and Weidenhagen (Naturwiss 1928, **16**, 654) has shown that this purified maltase at p_H 7 hydrolyses sucrose, the reaction being of the order of a maltose hydrolysis, whilst at p_H 4 6 which is the optimum for invertase action, no hydrolysis takes place The action is evidently that of a glucosidase acting on sucrose as an a glucoside

The hydrolysis of sucrose by invertase is rapid and complete, there is no evidence of reversion in highly concentrated solutions of the sugar.

A reaction which is claimed to be specific for sucrose (and raffinose) is the blue green colour given on shaking with diazouracil (Raybin, J. Amer. Chem. Soc. 1933, **55**, 2603).

Vicianose — glucose-6 β l arabinoside — is present in vicianin, violutin, gein, and has been synthesised by Helferich and Bredereck (Annalen, 1928, **465**, 166). It is related to melibiose in the same way as arabinose is to galactose.

Primeverose — a glucose 6 β d xyloside—is proving to be widely distributed in plant glycosides, being a constituent of primeverin, primulaverin, monotropin, gentiacaulin, and rhamnicosin. It is the sugar of the coloured anthraquinone glycosides It is perhaps formed in nature from gentiobiose *via* the uronic acid in the same way as xylose is formed from glucose. It has been synthesised by Helferich and Rauch (Annalen, 1927, **455**, 168)

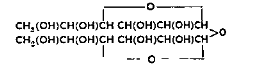
Strophantobiose — cymarose glucoside—is the sugar of Kombé strophanthin (Jacobs and Hoffmann, J. Biol. Chem. 1926, **67**, 609; **69**, 153; 1928, **79**, 531). It is hydrolysed to glucose and cymarose the deoxy sugar

$$CH_3\cdot[CH\cdot OH]_2\cdot CH(OMe)CH_2\cdot CHO.$$

Rutinose — glucose l rhamnoside — is the sugar of the glycosides rutin and datiscin (Charaux, Compt. rend. 1924, **178**, 1312; 1925, **180**, 1419).

Glucoxylose is a non reducing sugar of the trehalose type. It is present as a dibenzoyl derivative in the leaves and twigs of *Daviesia latifolia* (Power and Salway, J.C.S. 1914, **105**, 767, 1062).

Trehalose is aa diglucopyranose,



It is prepared from Trehala manna by extraction with 75% alcohol. The clarified and evaporated extracts crystallise on addition of 95% alcohol A yield of 20–25% is obtained (Harding, Sugar, 1923, 476).

It does not reduce Fehling's solution or form a phenylosazone. *It is hydrolysed by a special* enzyme, trehalase, present in most fungi and conveniently prepared from *Aspergillus niger*.

The best source is the resurrection plant obtainable in large quantities in the arid south-west of North America. This contains 2% of the sugar which is readily obtained crystalline

It was originally discovered in ergot, and has since been proved to be very widely distributed in fungi (Bourquelot). It apparently replaces sucrose in those plants which contain no chlorophyll and do not form starch.

It crystallises in lustrous rhombic prisms, m p. 97°, with $2H_2O$, becoming anhydrous at 130°. The anhydride has $[a]_D$ +197° without any mutarotation.

Theoretically there can exist three non-reducing disaccharides of the type of trehalose according as the two glucopyranose units are united through the reducing positions as the aa, $a\beta$, and $\beta\beta$ forms.

The natural sugar is the aa form. Fischer and Delbruck (Ber. 1909, **42**, 2783) synthesised the $\beta\beta$-form—*iso*trehalose—by the condensation of tetraacetylglucosidylbromide in the presence of silver carbonate. Haworth and Hickinbottom (J.C.S. 1931, 2847) have prepared what is probably the $a\beta$ form—*neo*trehalose—by the additive union of triacetylglucose-1:2-anhydride and tetraacetyl glucose in benzene solution.

The following table indicates the optical properties of the three substances:

	$[a]_D$
Trehalose . . .	+178° (hydrate)+197° (anhydrous).
Octaacetyltrehalose	+162° (in chloroform).
*neo*Trehalose . .	+95° (hydrate)+100° (anhydrous).
Octaacetyl*neo*trehalose.	+90° (in benzene).
*iso*Trehalose .	−39° (anhydrous).
Octaacetyl*iso*trehalose.	−17° (in benzene).

Synthesis of Disaccharides.

(a) By enzymes. In addition to the original synthesis of maltose claimed by Croft Hill,

(J.C.S. 1898, **73**, 634), Bourquelot *et al.* (Compt. rend. 1913, **157**, 732; 1916, **163**, 60; 1919, **168**, 1016; J. Pharm. Chim. 1920, [vii], **21**, 81) have synthesised gentiobiose, cellobiose, amannobiose, and two galactobioses. Robison and Morgan (Biochem. J. 1928, **22**, 1277) have observed the synthesis of trehalose by dried yeast.

(*b*) Chemical synthesis has been effected in a number of ways :

(1) By thermal condensation from α- or β-glucosan or galactosan (Pictet *et al.*, Helv. Chim. Acta, 1926, **9**, 806; 1927, **10**, 280, 588; 1928, **11**, 209).

(2) *Via* the 6-triphenylmethyl derivative of glucose. When the other groups are fixed by substituents the trityl group can be removed leaving a reactive hydroxyl on carbon 6 (Helferich, Annalen, 1926, **447**, 19; 1928, **465**, 166); thus gentiobiose, 6-β-galactosido-glucose and similar trisaccharides have been obtained from cellobiose, gentiobiose, and lactose.

(3) By means of the acetone sugars, Freudenberg *et al.* (Ber. 1927, **60**, 239; 1930, **63**, 1961; 1933, **66**, 27) has synthesised 6-galactose derivatives of mannose, galactose, lactose, and cellobiose, also mannosido-*l*-mannose.

(4) Cellobial is converted into 4-glucosido mannose and lactal into 4-galactosido mannose by means of benzoylperoxide (Bergmann, Ber. 1921, **54**, [B], 440).

A recent synthesis of gentiobiose is from the interaction of acetobromoglucose with 3:5-benzylidene-1:2-*iso*propylidene glucose (Brigl and Widmaier, Ber. 1936, **69**, [B], 1219). Another synthesis is that of 2-β-glucosido-α-glucose (Freudenberg and Soff, *ibid.* 1245).

Trisaccharides and Tetrasaccharides.

There exist sugars in which several different hexose or pentose units are combined (oligosaccharides). Little is known of the manner of their formation in plants or of their function. Interest centres in the order in which the constituent units are arranged and the manner in which they are broken down by enzymes. Only a limited number are known, but it is probable that others exist, particularly from among the saponin glycosides.

	Oligosaccharides.	$[\alpha]_D$
Reducing:		
Manninotriose	glucose-galactose-galactoside $6 \longleftrightarrow 1 \quad 6 \longleftrightarrow 1$	+167°
Rhamninose	galactose-rhamnose-rhamnoside	−41°
Robinose	rhamnose-galactose-rhamnoside	+5°
Scamnose	glucose-rhamnose-fucose	
Solanose	glucose-galactose-rhamnose	

	Oligosaccharides.	$[\alpha]_D$
Non-reducing:		
Raffinose	2,β-fructofuranose-1,α-glucose-6,α-galactoside	+104°
Melezitose	1,α-glucose-2,β-fructofuranose-6,α-glucoside	+88·7°
Gentianose	2,β-fructofuranose-1,α-glucose-6,β-glucoside	+33°
Stachyose	Fructofuranose-glucose-galactose-galactoside	+144°

Polysaccharides.

Much interest attaches to the formulæ of starch and cellulose. They are to-day regarded as chains of finite length and not as ring compounds. Both chemical and physical methods have been used to determine the size of the molecule. Importance attaches to the fact that they are built up from the disaccharides, maltose, and cellobiose, and that tri- and tetra-saccharide units are obtainable during their degradation.

From 1920 to 1926 it was assumed from the X-ray evidence that the molecule of cellulose was quite small and consisted of small structural units held together by some form of residual valency. A later interpretation of the X-ray diagram, due to Sponsler and Dore, was that ramie fibres consist of glucose residues linked by primary valencies (*see* Colloid Symposium Monograph, 1926, **4**, 174). The work of Staudinger (Helv. Chim. Acta, 1925, **8**, 41, 67) on the poly-oxymethylenes supported this view by analogy.

According to the molecular chain theory, a molecule of cellulose consists of a straight chain of glucoso-pyranose units united by β-glucoside linkages, each of which consequently has three alcoholic hydroxyls, namely 2:3:6, free. Such molecule should bear a reducing group on one end, whilst the other terminal glucose unit should have four alcoholic hydroxyl groups. Completely methylated cellulose on hydrolysis gives mainly 2:3:6-trimethylglucose with a small proportion of tetramethylglucose. All depends on whether the processes of acetylation, partial de-acetylation, and methylation used to convert cellulose into trimethyl-cellulose can be effected with little or no scission of the chain molecules. Haworth and Machemer (J.C.S. 1932, 2270, 2372) answer this question in the affirmative and claim that the chain length of about 200 glucose residues found for the methylated cellulose can be applied to cellulose.

Estimates made on the measurement of the reducing power either by means of copper or iodine give maximum values of 300 and 175 respectively.

On the physical side, measurements of chain length have been made by viscosity determinations. Staudinger (Naturwiss. 1934, **22**, 797, 813) gave the following figures for purified celluloses: ramie 1,000, cotton 750, sulphite-pulp 230–310, viscose rayons 100–250, industrial cellulose acetates 150–250.

By the ultra-centrifuge method the figures for cotton cellulose are 220–280 by one observer, and 1,300 by another.

The subject is still one of extreme controversy. Hess, Staudinger, and other Continental workers formulate cellulose as a thread with at least 2,000 glucose units and show that methylation in presence of air gives rise to degradation (Hess and Neumann, Ber. 1937, 70, [B], 728). Observations with hydrocellulose and oxycellulose confirm the view of the very large molecule and it would appear that Haworth's figure of 200 glucose units is an expression of a simplified unit, perhaps even a side chain, and that possibly a distinction must be drawn both for cellulose and starch between the chemical molecules and physical units. A fuller discussion will be found in the Annual Review of Biochemistry, 1938, vol 7

The chemical structure of all celluloses so far examined appears to be identical

When cellulose is treated with acetic anhydride, it is acetolysed: that is both acetylated and hydrolysed. Under certain conditions the main product is cellobiose acetate which, after correcting for losses, has been isolated in amount corresponding with 60% of cellobiose Under other conditions Hess and Dziengel *(Ber. 1935, 68, [B], 1594) have been able to* obtain at least 16% of cellotriose Cellotetraose and cellohexaose have also been described (Willstätter and Zechmeister, Ber 1929, 62, [B], 722, Zechmeister and Toth, Ber 1931, 64, [B], 854). These are the initial members of a long series of condensation products of β glucose

The molecular rotation of an oligosaccharide will be the sum of the rotation of the two terminal glucose groups which together make up cellobiose and those of the non terminal glucose units As the chain length increases the molecular rotation per glucose unit will asymptotically approach the value corresponding to the contribution of a non terminal glucose unit. This is actually the fact, indicating that trimethyl cellulose is similar in structure and configuration to the methylated oligosaccharides but differs in having a much greater chain length.

Much of the above applies to starch in which, however, the linkage of the glucopyranose molecules is α-, causing, it is believed, the molecular chain to take a spiral form. According to Staudinger and Eilers (Ber 1936, 69, [B], 819), this explains why starch of molecular weight 50,000 behaves in solution as if it were of the same chain length as a cellulose of 5,000.

In practice more than 99% of glucose is *obtained on complete hydrolysis of starch:* this disposes of the suggestion that the chain terminates in a carboxylic acid group

Haworth (J.C.S 1932, 2376), by the non reducing end unit method, concludes that the number of glucose units is of the order of 24–30.

Figures based on reducing power, which is quite distinct and measurable, are much higher, varying from 460–1,470 according to the sample. Measurement of osmotic pressure indicates 1,230, and of sedimentation 5,550 units.

These figures are much larger than Haworth's and it is probable that with starch some degradation takes place during the methylation process. In support of this view recent French work indicates that when acetylation is effected under *dry* conditions, it is impossible to introduce more than two acetyl groups into starch. Certain starches are associated with phosphoric acid of which the significance still remains a matter of conjecture.

On the hypothesis that pure unmodified starch, if there be such a substance, has a small reducing power, it will be obvious that in the early stages of hydrolysis a small increase in reducing power corresponds to a large decrease in average chain length. Since the viscosity of a solution of chain molecules is closely related to their average length, a rapid initial diminution in viscosity would be anticipated. This happening is well known with starch pastes and has been usually attributed to the formation of "soluble starch" by processes differing in kind from hydrolysis proper. It would appear such explanation is no longer correct and that soluble starch is a degradation product (*see* Richardson, Higginbotham and Farrow, Shirley Institute Memoirs, 1935, 14, 63).

The difference in viscosity between different starches may be in part accounted for by their differences in chain length. Sago starches have the shortest chains and farinas the longest. *The various starches exhibit different degrees of* resistance to enzyme action.

There is a good deal of evidence for what at first sight might be regarded as an anomalous fact that the two enzymes, α and β amylase, in attacking the same material, which appears to be some 60% of the starch molecule, produce two different final fission products, namely α- and β maltose.

This subject is still under active investigation (*see* Freeman and Hopkins, Biochem. J. 1936, 30, 442, 451).

Glycogen, the reserve carbohydrate of the animal organism in which it takes the place of starch, is a regular constituent of all developing cells. It is present in the liver up to 10% and in muscle. It also occurs in the lower fungi. It has $[\alpha]_D + 196°$ to $+ 197°$.

According to Haworth and Percival (J C S *1931, 1342; 1932, 2277*), the average minimum chain length is 12 glucose units. Fish liver glycogen appears to be identical with that from rabbit liver.

Galactogen from the snail is a galactose polymer having properties similar to glycogen

Mannans.—These are a group of polysaccharides composed of mannose or of mannose and glucose combined together, such poly*saccharides are frequently found together* in the same plant.

The vegetable ivory nut contains a mannan forming a triacetate and yielding at first a mannobiose on acetolysis (Pringsheim and Seifert, Z. physiol. Chem. 1922, 123, 205).

The glucomannan of Konjak powder (*Amorphophallus Konjak*) contains mannose and glucose in the ratio of 2 : 1. Salep-mannan from *Tubera salep* is composed of mannose units combined through the glycosidic groups as are the glucose units in starch (Klages and Niemann, Annalen, 1934, 509, 159; 512, 185; 1936, 523, 224).

The yield of tetramethylmannose obtained on hydrolysis of the methylated salep-mannan indicates a chain length of some 60 mannose

units (mol. wt. 12,000). This mannan is fairly soluble in water, whereas ivory nut mannans are insoluble. It is suggested that there is lateral coupling of the polysaccharide chains so that the particles are more nearly spherical. Mixed glucomannotriose and biose have been obtained from Konjak mannan.

Inulin is widely distributed as a reserve material in plants having tubers or tuberous or fleshy roots, particularly in the autumn in dahlia tubers, Jerusalem artichoke, chicory, garlic, onions, and other plants and bulbs.

The purest inulin has $[\alpha]_D$ −35° to −36°. It does not reduce Fehling's solution under three minutes' boiling. It is hygroscopic, but can be completely dried in a vacuum over phosphorus pentoxide (Berner, Ber. 1930, **63**, [B], 1356).

The present knowledge in regard to the constitution of inulin may be summed up quite briefly:

1. It is entirely composed of fructose molecules.
2. These fructose residues are exclusively of the γ-type.
3. These are linked in the form of a long chain.
4. The point of linkage is between the first carbon of one molecule and the second carbon of another molecule of fructose.
5. The number of fructose residues in the molecule is approximately 30, with a molecular weight of 5,000.

These conclusions have been reached as the result of the careful hydrolysis of methylated inulin. The main product is 3:4:6-trimethylfructose first identified by Haworth and Learner (J.C.S. 1928, 619), of which 85% of the theoretical amount has actually been isolated. Four additional substances have been shown to be present by Irvine and Montgomery (J. Amer. Chem. Soc. 1933, **55**, 1988), namely, methoxy-5-methylfurfural, which is merely a decomposition product of trimethyl-γ-fructose, trimethylglucose, tetramethyl-γ-fructose, and trimethylanhydrofructose.

Considerable importance attaches to the trimethylglucose. The actual amount present in the hydrolysate has been shown to be of the order of 3% (Jackson and Goergen, Bur. Stand. J. Res. 1929, 37) to 5% (Pringsheim and Reilly, Ber. 1930, **63**, [B], 2636), but it is now clear that the conversion of γ-fructose into the corresponding glucose derivative takes place under the conditions adopted to hydrolyse trimethyl inulin.

A number of polymers of fructose have been found to occur naturally. The *levan* obtained by the action of *β-mesentericus* on sucrose or on raffinose consists of chains of fructofuranose units joined through positions 2 and 6 (Hibbert, Tipson, and Brauns, Canad. J. Res. 1931, 4, 221) having a chain length of 10–12 units (Challinor, Haworth, and Hirst, J.C.S. 1934, 676). The same levan has been found as reserve carbohydrate in meadowgrass (*ibid.* 1560).

Irisin, a polyfructose conveniently obtained from the rhizomes of *Iris pseudacorus*, is claimed to contain 2:4-anhydrides of fructofuranose (Schlubach, Knoop, and Liu, Annalen, 1934, **511**, 140).

Pentosans.—These important constituents of the woody tissues of plants are determined by conversion into furfuraldehyde under standard conditions. The best known is *xylan*, which forms 30% of esparto cellulose. This was long thought to be wholly composed of xylose, but has been shown to contain some combined arabinose (Haworth, Hirst, and Oliver, J.C.S. 1934, 1917).

It is considered that the arabinose is a terminal unit associated with about 16 xylose units which are pyranose in structure though other more complex structures are possible.

Fuller details of the questions discussed will be found in "The Carbohydrates," by E. F. and K. F. Armstrong, Longmans, 1934, and "The Glycosides" by the same authors, Longmans, 1931. Physical constants of sugar derivatives are contained in Vogel and Georg., "Tabellen der Zucker und ihrer Derivate," Berlin, 1931.

E. F. A.

CARBOHYDRAZIDE (has been called *Carbazide*),

$$CO\cdot(NH\cdot NH_2)_2,$$

obtained by heating alkyl esters of carbonic acid with hydrazine hydrate at 100°. It forms colourless crystals, m.p. 152°–153°, and combines with 2 mols. benzaldehyde to form the compound $CO(NH\cdot N{:}CHPh)_2$, m.p. 198° (Curtius and Heidenreich, Ber. 1894, **27**, 55; J. pr. Chem. 1895, [ii], **52**, 454).

CARBOLIC ACID, phenol, $C_6H_5\cdot OH$.

Occurrence.—Carbolic acid occurs in small quantities in castoreum (Wöhler, Annalen, 1848, **67**, 360), in urine (Städeler, *ibid.* 1851, **77**, 18), and is a constant product of the putrefaction of albumen (Baumann, Ber. 1877, **10**, 685). It is formed when organic substances are strongly heated, and is contained in the tars obtained by the dry distillation of bones, wood (Duclos, Annalen, 1859, **109**, 163), shale (brown coal) and coal (Runge, Pogg. Ann. 1834, **31**, 69; **32**, 308; Laurent, Ann. Chim. Phys. 1841, [iii], **3**, 195).

Preparation.—In Great Britain phenol was, until 1910, obtained exclusively from gas works tar. With the development of the by-product coke oven, commencing about that date, tar from this source was similarly treated for recovery of phenol. During the period 1916–1918 three plants producing synthetic phenol from benzene were in operation, and from 1919 to 1936 coal tar again formed the only source, the annual production in 1935 being about 3,000 tons. In the latter year a synthetic plant commenced production. In Germany, coke oven tar is the main source, but synthetic plants are also in operation. The pre-war production of 2,400 tons per annum increased to 4,826 tons in 1933, of which 3,500 tons were obtained from coal tar. Total production from tar, synthetic processes, and recovery from ammoniacal liquor is now (1937) of the order of 10,000 tons per annum. In 1935 the total production was not far from 9,000 tons. In U.S.A. the production from coal tar rose from 450 tons in 1914 to 1,350 tons in 1929, and by 1935 to between 5,000 and 6,000 tons. The production of synthetic phenol in U.S.A. reached a maximum at 44,600 tons in 1918, after which most of the plants were closed down

until 1923, since when output has increased to 9,000 tons in 1929 and to over 20,000 tons in 1935, mainly to meet the demand from the bakelite resin industry. The hydrogenation of coal for the production of motor spirit yields phenol and cresols as by-products, but no production figures are yet available.

The phenol content of coal tars depends upon the method of carbonisation and the coal used; typical figures are: average English gas works tar, 0·4–0·8%; Ruhr coke oven tar, 0·18%; Silesian coke oven tar, 0·41%; Saar coke oven tar, 0·59%; German gas works tar, 0·89%. For low temperature tar, figures from 0·1 to 1·5% have been quoted (Wiltshire, J.S.C.I. 1931, 50, 125T), the hydrogenated tar containing 4·9%. The preparation of carbolic acid from coal tar is effected by washing the light oils and carbolic oil, that is, the oils distilling below 230°C., with a solution of caustic soda, sp. gr. 1·075–1·100, when the tar acids (phenols) are dissolved as sodium compounds and form a heavy solution upon which the hydrocarbon oils float. The use of a stronger solution of caustic soda increases the quantity of naphthalene dissolved, and is not recommended. As phenol in tar is usually accompanied by 3 to 4 parts cresols and xylenols, if it is desired to extract the whole of the carbolic acid and as little as possible of its homologues, the oils are washed fractionally. For example, a quantity of caustic soda solution more than enough to extract all the carbolic acid, but insufficient to take up all the cresylic acid, is employed and the phenate and cresylate of soda solution drawn off is used to wash another portion of oil when the cresylate of soda is decomposed and the cresylic acid is partly replaced by phenol. In most works, however, practically the whole of the phenols contained in the light oils and carbolic oil fractions is extracted, and after separating the phenols by one of the ways described later, the mixture of carbolic and cresylic acids obtained is separated by fractional distillation. If there is a good market demand for cresylic acid the higher boiling creosote fractions may also be washed. The phenate of soda solution drawn off from the oils is purified by blowing steam through it to remove naphthalene, neutral oils, and pyridine bases, the operation being continued until the condensed distillate ceases to have a milky appearance.

The solution is then decomposed by carbon dioxide, normally obtained from a coke producer or from a lime kiln. A few small works still employ the older method of decomposing limestone with sulphuric or hydrochloric acid. The free tar acids float to the surface and are separated and treated with sufficient sulphuric acid to neutralise the dissolved alkali, and simultaneously reduce the water content to below 15%. The alkali content of the crude tar acids before acid treatment may be reduced by treatment with further CO_2, thus forming the less soluble bicarbonate.

The separated solution of sodium carbonate, which contains about 1% of carbolic acid, is recausticised with lime and used again to wash a further quantity of oil. The carbolic acid remaining in solution is thus recovered, inasmuch as it goes forward with the regenerated caustic soda and is regained in the next washing, and the total use of Na_2CO_3 in the process is reduced to about 1-lb. per gallon of crude phenols recovered. The crude carbolic acid thus obtained contains, besides phenol (carbolic acid), about 14–15% of water and variable quantities of cresylic acid. It is brought into commerce in a number of qualities, the most important of which is known as "60's," being a product which when examined by Lowe's test (p. 308) gives a crystallisation test not lower than 60°F. This product is further subdivided into grades according to the amount of impurities (neutral oils and pyridine bases) present. A dehydrated quality contains less than 3% water and the distilled quality also contains less than 3% water, and shows not more than 2% of pitch residue in the distillation test as compared with figures of up to 6% in the ordinary quality (cf. B.S.I. specifications 515 and 516 of 1938).

The preparation of pure phenol from the crude product involves first a distillation from a wrought iron still, usually fitted with a fractionating column, water comes over first, and then crude phenol, which is collected apart so long as the distillate crystallises on cooling to 15°C., finally crude cresylic acid distils over, a pitch residue being left in the still. The crude phenol is then redistilled from a steam coil-heated vacuum still fitted with an efficient bubbling hood or ring-packed fractionating column, the condenser and attached pipes on this still being of enamelled cast iron, tin, nickel, or monel metal; silver was formerly used. The distillate fraction having a minimum crystallising point of 35°C., is allowed to cool and crystallise, and the crystals are separated from the liquid portion either in a drainer or in a centrifugal machine. The liquid portion is reworked through the still with the next batch. The drained crystals may be treated with a small quantity of concentrated sulphuric acid and potassium dichromate and redistilled. Other purifying reagents which have been proposed are aromatic sulphonic acids (U.S.P. 1824864), sodium borate (B.P. 276216), and alkali carbonates (U.S.P. 1931057). In some cases the separation of the last traces of cresylic acid is effected by adding a small quantity of water and cooling the mixture, when phenol hydrate crystallises out; this is separated from the liquid portion which contains the cresylic acid, and the crystals are redistilled. Water comes over first, and then the vapour temperature rises rapidly and pure phenol distils over (see Rhodes, Wells, and Murray, Ind. Eng. Chem. 1925, 17, 1199). Tin or nickel storage vessels are employed and the product is despatched in tinned or galvanised iron drums.

Synthetic phenol is now made by two methods:

(1) By sulphonating benzene, neutralising the resulting benzenesulphonic acid and fusing the sodium salt with caustic soda. Normally, acid of 99–100% strength is employed, the temperature of sulphonation being 100°–120°C. The sulphonation charge is diluted with water, neutralised with milk of lime, and filtered on a rotary filter or through Dorr thickeners. The calcium phenate is decomposed with sodium

carbonate and the separated carbonate is used to neutralise a further charge of sulphonate. For the fusion stage, 25–30% excess NaOH is employed in direct heated pots at 340°C., decomposition begins energetically at 320°. The yellowish-brown mass is treated with sufficient water to yield a solution of sodium phenate containing 10% sulphite, leaving the bulk of the sulphite undissolved. The solution contains 16% phenol, and CO_2, SO_2, or H_2SO_4 is added and the free crude phenol then separated and redistilled. The sulphite can be employed to convert the calcium sulphonate into sodium sulphonate and also for the production of SO_2 for the separation of the phenol. Killeffer (Ind. Eng. Chem. 1924, 16, 1066) describes a modern sulphonation process and costs data are given in D.E.S. Tech. Records No. 6. The process has been improved by increasing the yield in the fusion stage (absence of air), by eliminating the use of lime and utilising the Na_2SO_3 by-product. Rhodes, Jayne, and Bivins (Ind. Eng. Chem. 1927, 19, 804) state that by fusion of the sodium sulphonate with 15% excess NaOH at 350° in the absence of air (superheated steam passed over the melt) a yield of 96% of the theoretical is obtained. In presence of air, formation of *o*- and *p*-diphenols lowers the yield to 87%, and if too little NaOH is used, diphenylether and thiophenol are formed (*see also* B.P. 218034, 1923).

(2) By chlorinating benzene and heating the resulting chlorbenzene with caustic soda solution under high pressure, Aylsworth (U.S.P. 1213142, 1917) showed that decomposition of the chlorbenzene can be carried out continuously if the mixture is passed through a tube still under pressures of 2,000–4,000 lb. per sq. in. at 340°–390°, *i.e.* at temperatures which approximate to the critical temperatures of water (372°) and chlorbenzene (362°). Hale and Britton (Ind. Eng. Chem. 1928, 20, 114) investigated this reaction, and the Dow Chemical Co. patents and process are based on their work (U.S.P. 1737841, 1737842, 1744961, 1756110, 1856021). Hydrolysis is carried out in a welded coil autoclave consisting of 1 mile of $\frac{1}{2}$-in. tube of wall thickness $\frac{1}{4}$-in., pressures up to 4,000 lb. per sq. in. at 340°–350° being employed. Diphenyl oxide or diphenyl is employed as heat transmitting agent. Diphenyl oxide is added to the reaction mixture and is mutually miscible with the chlorbenzene and facilitates emulsification with the caustic solution. The formation of further diphenyl oxide and other side reactions are thereby repressed. Hydroxydiphenyl, mainly the para-compound, is the chief constituent of the waste tar formed, and is apparently to be traced to phenol acting in its tautomeric form. Phenol yields of the order of 93% are claimed. Caustic soda may be replaced by sodium carbonate in presence of a copper catalyst.

An attempt has been made to simplify the high-pressure chlorbenzene process by hydrolysis in the vapour phase with steam under ordinary pressures, the mixed vapours being passed through a heated porous catalyst at 700°. I.G. Farbenind. A.-G. (B.P. 288308 and 308220) claim increased yields using the same reaction, certain metals such as Ca, Ni, Co or metallic oxides being added to a silica gel mass (*see also* Prahl and Mathes, Angew. Chem. 1934, 47, 11; Raschig, B.P. 362817, 387832, 410331).

Manufacture through nitrobenzene-aniline: by direct oxidation of benzene (U.S.P. 1547725); or by the action of water and air on benzene in the presence of an alkali and certain metallic oxide catalysts (U.S.P. 1595299); and by elimination of the methyl group from cresols has also been investigated (Kahl, B.P. 427145).

New reagents have been suggested for the extraction of phenols from tar oils, particularly those obtained by low temperature processes. Stanier (B.P. 344614) employs triethanolamine, the extract being diluted with water preferably followed by saturation of the diluted mixture with CO_2 or H_2S. The free base is recovered by concentration of the phenol-free solution. Perilhou (B.P. 338638) employs an aqueous solution of alkali carbonates under pressure and at temperatures above 100°C. with continuous escape of CO_2. The phenates are isolated and decomposed with CO_2. Miller (U.S.P. 1819687) employs milk of lime, and alcohol and ammonia have also been employed, particularly in the treatment of low-temperature tar oils (Jarry, Compt. rend. 1932, 194, 614).

The ammoniacal liquor from gas and by-product coke ovens is another source of phenol, and since 1927 a number of plants have been put into operation in U.S.A. and in Germany. (Wiegmann, Glückauf, 1932, 68, 40; Berthelot, Rev. Mét. 1933, 30, 488). The first British plant began operation in Manchester in 1931 (Gas J. 1931, 195, 468). These processes yield a small margin of profit but have been developed mainly with a view to reduction of toxicity of the ammonia still effluents. The concentrated liquor is extracted with benzene and the phenols recovered either by fractional distillation or by extraction with caustic soda solution and acidification of the resulting phenates. The Koppers process recovers the phenols from the partly distilled liquor in the ammonia still—the liquor being extracted with benzene before passing to the liming leg of the still. At Manchester the liquor is concentrated in the foul gas main to 14–18% NH_4Cl content, and then washed with benzene. The higher tar acids and benzene are recovered from the effluent by means of active charcoal. Robinson and Parkes (B.P. 260686) recover the tar acids by acidifying the liquor with CO_2, treating with active charcoal, separating the latter, and steaming off the tar acids. The use of tricresylphosphate as an extracting medium has been patented. The ratio phenol : cresols in the recovered product is stated to be 2 : 1. Recent information indicates that 1,800 metric tons per annum of pure phenol are recovered in Germany from gas and coke oven liquors, equivalent to about 15% of the total output.

"Liquefied phenol," phenol, 80%, w/w with water (limits 78·5 to 81·5). Specific gravity about 1·063 (B.P.C. 1934), is to be distinguished from the commercial liquid carbolic acid, which consists essentially of a mixture of the three isomeric cresols.

Properties.—Pure phenol (carbolic acid) crystallises in long, colourless needles, which

tend to turn pink on storage; has a characteristic not unpleasant aromatic odour, and an astringent but sweetish taste. The crystallising point is given as 41·0° corr. (Dawson and Mountford, J.C.S. 1918, 113, 937), 40.8° corr. (Rhodes and Markley, J. Physical Chem. 1921, 25, 527), 40.92°±0.1° corr. (Hill and Malisoff, J. Amer. Chem. Soc. 1926, 48, 921); *see also* Fox and Barker (J.S.C.I. 1917, 36, 842; 1918, 37, 268), and Stratton and Partington (Phil. Mag. 1922, 43, 326). The standard commercial product has crystallising point 39.5°–40.8° (*see* B.S.I. Specn. No. 523 of 1938). Phenol, B.P. must give a clear solution in 13 parts of water at 15.5°C., contain not less than 98% C_6H_5OH, and have crystallising point about 40°C. The specific gravity of phenol at 18°C. is 1.065 (Laurent); d_4^{25} 1.0710 (Dawson and Mountford (*l.c.*)) d_{40}^{40} 1.0586 (Richardson and Robertson, J.C.S. 1928, 1775), while d_t between 40° and 60° has been quoted as $1.09226-0.000858t$. Its expansion with temperature $t°$ at 760 mm pressure is stated by Kopp as follows:

$$V_t=1+6744\times10^{-7}t+172\times10^{-8}t^2+50408\times10^{-14}t^3.$$

The freezing points of phenol containing 0, 0.5, 1·0, 1·5, and 2.0% of water are 40.8°, 38.8°, 36.9°, 35.0°, 33.2° respectively. B.p. is 73.5°/10 mm., 120.2°/100 mm., 159.7°/400 mm., 167°/500 mm., 181.7°/760 mm. Refractive index n_D^{21} 1·5509, n_D^{45} 1·54018. The latent heat of fusion has been measured by Stratton and Partington (*l.c.*), and found to be 28.9 g. cal. per g. Data for the two crystalline forms are given by Bridgman (Proc. Amer. Acad. Arts. Sci. 1915–1916, 51, 111). The heat of combustion is 734·2 kg.-cal./mol. (Berthelot and Luginin, Ann. Chim. 1888, [vi], 13, 329). Surface tension at 50°C., 37·74; at 90°C., 33.35 (Berczeller, Biochem. Z. 1914, 66, 173). Heat of solution −10.9 kilo joules per mol. solute.

Phenol coagulates albumin, is a powerful antiseptic, being more effective against aerobic than anaerobic bacteria, acts as a caustic on the skin, and is very poisonous. Its local action is much influenced by the solvent—a solution in pure glycerol and alcohol is scarcely caustic. Phenol burns on the skin should be washed freely with alcohol and subsequently treated as ordinary burns (Allen).

The critical solution temperature and concentration in water are variously given as 65.3°, 36.5% (Bailey, J.C.S. 1925, 127, 1952); 65.85°, 34·23% (Hill and Malisoff, *l.c.*); 65.5°, 34.0% (Dolique, Compt. rend. 1932, 194, 289). The effect of the addition of small quantities of benzene, naphthalene, or pyridine is to raise the critical solution temperature, but it is lowered by resorcinol, pyrocatechol, or hydroquinone (*see also* Bull. Sci. Pharmacol. 1932, 39, 129). For effect of salts on the critical solution temperature, *see* Patterson and co-workers (J. Physical Chem. 1925, 29, 295; J.C.S. 1925, 127, 2544). Hill and Malisoff (*l.c.*) give the following figures for the mutual solubility of phenol and water:

Temp.	Phenol phase.		Water phase	
	% wt. phenol	Density	% wt. phenol	Density
20°	72·16	1·0541	8.36	1·0018
25°	71·28	1.0469	8.66	1·0045
30°	69.90	1·0429	9.22	1·0039
35°	67·63	1.0405	9.91	0.9974
57·3°	—	—	14.87	—
62.55°	51.87	—	—	—
65.79°	—	—	27·77	—

Rhodes and Markley (*l.c.*) give the hydrate as $2C_6H_5{\cdot}OH,H_2O$, m.p. 15.9°. The hydrate is not readily isolated, but can be obtained by seeding with hydrate crystals or by cooling to very low temperatures. It forms eutectics with phenol and ice respectively. The solid phase which ordinarily appears when a mixture of phenol and water is cooled is the metastable anhydrous phenol, due to the tendency towards suspended transformation.

The coefficient of reciprocal miscibility of phenol and water steadily increases with the addition of alkali hydroxides to the water. Acids and salts of the stronger acids cause a diminution of the coefficient, and the same holds good for alkali carbonates (Dubrisay, Tripier, and Toquet, Compt. rend. 1918, 167, 1036). The influence of neutral salts on the partition of phenol between benzene and water, where S=salt concentration, is given at 25° by $B=2.272\times10^{\beta S}C+37{\cdot}71\times10^{3\beta S}C^2$, where B and C are molar concentrations of phenol in benzene and the aqueous layers respectively, and β is a constant characteristic of the salt (Endo, Bull. Chem. Soc. Japan, 1927, 2, 124). Boyd (J.C.S. 1915, 107, 1538) gives the ionisation constant $K_a(25°)=1{\cdot}15\times10^{-10}$. Phenol is soluble in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerol, olive oil, chloroform, carbon disulphide, etc.

A. Hagemann (Z. angew. Chem. 1929, 42, 503; 1931, 44, 221) has studied the thermal decomposition of phenol, the main products being *cyclo*pentadiene, naphthalene, carbon monoxide and methane. In the presence of hydrogen, benzene is also formed.

Phenol is readily attacked by tin; no action occurs at 30°C., but above the temperature of boiling water benzene and SnO_2 are formed. Boiling anhydrous phenol dissolves aluminium with evolution of hydrogen and formation of $Al(OC_6H_5)_3$, but the action is inhibited by presence of water; the phenate decomposes on heating to form diphenyl ether. The most resistant metals are nickel, silver, and nickel and chromium-nickel steels of the 18/8 type (Rhodes, Riedel, and Hendricks, Ind. Eng. Chem. 1934, 26, 533). Two isomeric mononitrophenols are obtained by the action of dilute nitric acid (sp. gr. 1.34); at lower temperatures the *para*- and at higher temperatures the *ortho*-derivative appears to be chiefly formed (Goldstein, Ber. 1878, 11, 1943). By the further action of nitric acid, dinitrophenol (Kolbe, Ber. 1871, 4, 147) and trinitro phenol (picric acid)

(Schmitz and Glutz, Ber. 1869, 2, 52) are formed.

Chlorine and bromine convert phenol at ordinary temperatures into mono-, di-, and tri-substitution derivatives, and at higher temperatures or in the presence of halogen carriers, such as antimony pentachloride, etc., into tetra- and penta- derivatives. The nitro-, chloro-, and bromo- derivatives are fairly strong acids, and the acid character increases with the number of nitro-groups or chlorine or bromine atoms introduced into the molecule. Iodine yields mono- and di-derivatives in the presence of mercury (Hlasiwetz and Weselsky, Ber. 1869, 2, 524) or iodic acid (Körner, Annalen, 1866, 137, 213). Sulphuric acid converts phenol into two isomeric monosulphonic acids (Kekulé, Z. f. Chem. 1867, [2], 3, 197); at ordinary temperatures the *ortho*- and at higher temperatures the *para*- acid is the chief product. When heated with ammonium zinc chloride at 280°–300°, phenol yields aniline, together with diphenylamine and phenyl ether (Merz and Weith, Ber. 1880, 13, 1299). When fused with caustic potash, salicylic acid, *meta*-hydroxybenzoic acid and two isomeric diphenols are formed (Barth and Schreder, Ber. 1878, 11, 1332), whilst fusion with caustic soda results in the formation of pyrocatechol, resorcinol, and phloroglucinol (*idem.* Ber. 1879, 12, 417). The behaviour of sodium and potassium phenates when heated in a current of carbon dioxide has been studied by Kolbe (J. pr. Chem. 1874, [ii], 10, 89; *cf. also* Schmitt, *ibid.* 1885, [ii], 31, 397; D.R.P. 29939/1884); with sodium phenate the reaction commences below 100°, is most rapid and complete about 180°, and continues up to the temperature of the decomposition of sodium salicylate with the formation of that compound as sole product, but with potassium phenate salicylate is formed only at temperatures below 150°, whilst at higher temperatures the isomeric potassium *para*-hydroxybenzoate constitutes almost the entire product; in these reactions, one-half of the phenol is recovered. When phenol is heated with phthalic anhydride and a dehydrating agent, such as zinc chloride or sulphuric acid, it yields phenolphthalein (Baeyer, Ber. 1876, 9, 1230; Annalen, 1880, 202, 68). Phenol distils without alteration with phosphoric acid, but reacts with phosphoric anhydride at 40° to form monophenyl and diphenyl phosphates.

Sodium and potassium phenates may be readily crystallised from their solutions. Calcium phenate is formed by dissolving phenol in milk of lime. On boiling the aqueous solution half the phenol is liberated and the basic salt $C_6H_5{\cdot}OCa{\cdot}OH$ is precipitated. Like aliphatic alcohols, phenol forms both ethers and esters (*e.g.* anisole, methyl phenate, and *salol*, phenyl salicylate).

Reactions.—(1) In aqueous solution phenol gives a violet colour with ferric chloride (avoiding excess); this, however, is developed neither in very dilute solutions nor in the presence of alcohol; most mineral and organic acids, acetates and ether also interfere. Other compounds also give the same coloration, and therefore the test can only be employed as a control reaction; limit of sensitiveness, 1 in 1,500. (2) The aqueous solution, on treatment with ¼ vol. of ammonia and then with a few drops of an aqueous solution of bleaching powder (1 part in 20 parts of water), gives either at once or on standing a blue coloration; limit of sensitiveness 1 in 4,000 (Salkowski, Z. anal. Chem. 1872, 11, 316). (3) Fresh bromine water, added to an aqueous solution of phenol, gives either at once or on standing a yellowish-white flocculent precipitate of tribromophenol, limit of sensitiveness 1 in 43,700 (Landolt, Ber. 1871, 4, 770), 1 in 80,000 by recognisable cloudiness with slow crystalline separation (Lunge). Phenol homologues give similar reactions. (4) A solution of phenol assumes a deep red colour when heated at 100° with five-sixth its bulk of Millon's reagent (a solution of basic mercury nitrate containing nitrous acid); the reaction is distinct with 1 in 60,000 and still appreciable with 1 in 200,000. β-Naphthol gives a similar reaction (Chapin, Ind. Eng. Chem. 1920, 12, 771). (5) Rodillon (J. Pharm. Chim. 1921, [vii], 23, 136) gives the following characteristic reaction for phenol:—if 10 c.c. of a solution containing phenol are treated with a drop of 10% sodium nitrite solution and then poured on the surface of conc. H_2SO_4, a coloured zone (red above, green below) appears at the junction of the two liquids.

Quantitative Estimation.—The exact phenol content of commercial crystals is determined from the crystallising point of the anhydrous sample (*see* "Standard Methods of Analysis of Tar and its Products"). Typical figures are:

Crystallising point, °C.	Fractional content *of phenol.*
41·0	1·000
40·5	0·991
40·0	0·983
39·5	0·974
38·5	0·957
35·0	0·896
30·0	0·809
27·0	0·757

The solubility in water, the colour, and the odour are also noted.

The determination of phenol in liquefied phenol is based on the reaction with standard bromine solution. The precipitate formed with bromine consists of tribromophenol, and under certain conditions partially of tribromphenol bromide (*see* Koppeschaar, Z. anal. Chem. 1876, 15, 233; Beckurts, Arch. Pharm. 1886, [iii], 24, 562). The reactions involved are the following:

I. $C_6H_5{\cdot}OH+3Br_2=C_6H_2Br_3{\cdot}OH+3HBr$

II. $C_6H_5{\cdot}OH+4Br_2=C_6H_2Br_3{\cdot}OBr+4HBr$

III. $C_6H_2Br_3{\cdot}OBr+2KI=C_6H_2Br_3{\cdot}OK+KBr+I_2$

In the modern standard method the following reagents are employed: (*a*) Decinormal bromide-bromate solution made by dissolving 10 g. of potassium bromide and 2·784 g. of potassium bromate in distilled water and making up to 1,000 c.c.; (*b*) decinormal sodium thiosulphate solution. For the titration, 25 c.c. of the phenol solution (1·5 g. in 1,000 c.c.) are treated with 30 c.c. of the *N*/10 bromide-bromate

solution in a stoppered bottle and 5 c.c. of concentrated hydrochloric acid are added. The contents of the bottle are repeatedly shaken for half an hour, after which the bottle is allowed to stand for 15 minutes, treated with 5 c c of a 20% *w/v* aqueous solution of potassium iodide, shaken, and finally titrated with the thiosulphate solution to estimate the iodine liberated. One c c of *N*/10 bromide-bromate solution is equivalent to 0 001568 g. of phenol. The method is accurate when solutions of pure phenol, or mixtures from which the pure phenol can be separated, are to be tested, but it fails in the presence of cresols or other phenols (*see also* Messinger and Vortmann, Ber. 1890, 23, 2753 ; Skirrow, J.S C.I. 1908, 27, 58 ; Schryver, J.S C.I. 1899, 18, 553 , Weiss and Downs, Ind Eng. Chem. 1917, 9, 569 , Fox and Barker, J.S.C.I. 1917, 36, 842T, *ibid* 1918, 37, 265T , Hoffert, J S.C.I. 1922, 41, 334T) For a full discussion on the bromate-bromide method see Callan and Henderson (J.S C.I, 1922, 41, 161T)

Pieters (Chem. Weekblad, 1930, 27, 334), Bach (Gas-u. Wasserfach, 1931, 74, 331, and Scott (Ind. Eng. Chem. [Anal] 1931, 3, 67) have published methods for determination of phenol in effluent liquors.

Fox and Gauge (J S C.I 1920, 39, 260T) add to the alkaline solution containing the phenols a freshly prepared solution of diazotised sulphanilic acid and estimate the coupled phenols colorimetrically. Millar and Urbain (Ind. Eng. Chem. [Anal.] 1930, 2, 123) employ a modified form of this method, the phenol being quantitatively destroyed by chromic acid and thus determined by difference.

Crude carbolic acid "60's" (*see* p. *304*) is evaluated by determination of the water content, specific gravity, residue on distillation, neutral oils and pyridine bases present, and by the modified "Lowe's" test The latter is performed as follows. 100 c c. of the sample are slowly distilled from a distillation flask, bulb capacity 170 c c, and the receiver is changed when all the water and 10 c c. of clear distillate (oil) have collected. The rate of distillation is now increased to 1 drop per second and 62½ c c. are collected; the receiver is then changed and distillation continued until pitching occurs. The distillate of 62½ c.c. is then warmed, well shaken, and 20 c.c. placed in a small boiling tube surrounded by a larger boiling tube forming an air bath. The larger tube is immersed in a water bath at a temperature not more than 3°F. below the anticipated crystallising point. The contents of the inner tube are slowly cooled to about 0 5°F. above the expected crystallising point as previously approximately determined on a separate portion of the distillate and then seeded with a crystal of phenol. The highest temperature recorded by the thermometer after crystallisation has commenced is taken as the crystallising point. For accurate results it is necessary to employ standard apparatus and follow carefully the standardised conditions (*cf.* B S.I. specification No. 515/1938, S.T.P.T.C. Handbook, 2nd ed.). The standard 60's carbolic acid contains 45–46% phenol, 15% water, 6% pitch, and the product is sold on a sliding scale basis related to the crystallising point as above determined If the crystallising point is below 45°F, the product is graded as crude cresylic acid The product is then tested by submitting 250 c c of the sample to a fractional distillation. When the thermometer records a temperature of 170°, the distillation is stopped, the phenols in the aqueous distillate salted out and returned to the distillation flask, and the distillation continued, collecting separately (*A*) a fraction to 195°, and (*B*) a fraction between 195° and 205°C. Fraction (*B*) is redistilled and the distillate to 197° is added to fraction (*A*). To this combined distillate is added four times its weight of phenol, the mixture is heated to remove traces of moisture, and the crystallising point is then determined. The phenol content is then ascertained by reference to a table. If the amount of sample available is small, or when the phenol content of the sample is less than 20%, the colorimetric method due to Chapin (Ind Eng. Chem. 1920, 12, 771) may be employed.

Uses.—Phenol has powerful antiseptic properties, and was formerly largely used as a disinfectant. Its widest use now is in the synthetic resin (bakelite, *q.v.*) industry; phenol condenses with formaldehyde in the presence of acids and alkalis to form solid resin-like bodies which are capable of polymerising under the action of heat into hard non fusible, relatively inert products, which are good insulators and which resist chemical action. The phenol resins yield moulding powders which give less shrinkage as the moulding cools than the corresponding cresol powders, and for this reason are preferred where strict size limits in the finished article are essential.

The more important medicinals prepared from phenol are aspirin, salicylic acid, methyl salicylate, sodium salicylate, and phenolphthalein, in this order. Phenol, through its nitro- and amino- compounds, particularly of salicylic acid, is used in the aniline dye industry. The trinitroderivative, picric acid, was formerly much used as a high explosive (lyddite). Other uses are for perfumes, photographic chemicals, plasticisers (triphenyl phosphate and *cyclo*hexanol), detergents (*cyclo*hexanol), and synthetic tanning materials. Phenol has recently been used as an addition agent in copper plating for the purpose of refining the grain size of the deposit. A new demand has arisen in the modern solvent refining methods for lubricating oils (J. Dickinson, Oil and Gas J. 1935, 33, [51], 16). Phenol is also used industrially in the form of sodium phenate. F. M. P.

CARBOLINEUM. A brown distillate of coal tar used for preserving wood; anthracene oil (b p. 250°–400°) is one of the ingredients.

CARBO OVEN *v.* CARBON; WOOD CHARCOAL.

"CARBON" (CARBONADO) *v.* ABRASIVES.

CARBON. Sym. **C.** Atomic number *6*; atomic weight 12 00, two isotopes of masses 12 and 13. It occurs in nature in the free state, and very abundantly in combination, notably in the form of carbon dioxide and carbonates, and as an essential constituent of all organic matter, *e g.* plant and animal tissues, coal, etc. It is twelfth in the series of the relative abun-

dance of elements in the earth. It is a tasteless, odourless solid, and exhibits great diversity in the physical characteristics of its allotropic forms, diamond, graphite, and charcoal. It vaporises without melting at 3,500°–4,000°C. (Violle, Compt. rend. 1892, **115**, 1273; 1895, **120**, 868; Crookes, Proc. Roy. Soc. 1905, **76**, A, 458; Moissan, "Le Four Électrique," Paris, 1897, p. 159); 3,467° (Warmuthy, Wiss. Veröff. Siemens-Konz. 1928, **7**, 317). In nearly all its compounds carbon is tetravalant; the characteristic property of union between carbon atoms in chains or rings leads to the formation of a vast number of organic compounds. It is in general chemically inert at ordinary temperatures, but lampblack and charcoal take fire when introduced into fluorine. It unites with hydrogen at very high temperatures to form hydrocarbons (Bone and Coward, J.C.S. 1908, **93**, 1975; 1910, **97**, 1219; Pring and Hutton, *ibid.* 1906, **89**, 1591; 1910, **97**, 498). At high temperatures it is dissolved by the alkaline earth carbides and by platinum, rhodium, iridium, and palladium (Kahn, Compt. rend. 1906, **143**, 49; 1907, **144**, 197; Moissan, *ibid.* 1896, **122**, 1479; 1896, **123**, 16). It reduces alumina at the temperature of the electric arc. The affinity of carbon for oxygen at high temperatures is responsible for its widespread use as a fuel, and as a reducing agent in metallurgy.

Diamond was shown to be combustible by members of the Accademia del Cimento in 1694, and Lavoisier in 1772 found that it burnt in air to produce a gas which turned lime-water milky. Tennat in 1797 showed that this gas was carbon dioxide, and Dumas and Stas in 1841 proved that diamond was pure carbon in colourless crystals associated with as little as 0·05–0·2% of ash. Graphite, as its synonyms, blacklead and plumbago, indicate, was long considered to be a kind of lead and was often confused with molybdenite until C. W. Scheele (1779) demonstrated its true nature as a kind of mineral charcoal.

The specific gravity of diamond is 3·3–3·5, whilst that of graphite is 2·1–2·3. Diamonds occur sparingly in river beds or embedded in "blue clay"; as found, they are rounded stones resembling gum arabic in appearance, but are cut for gems into shapes such as the rose and the brilliant which bear no relation to their natural crystalline form. They are sold by the carat, the exact value of which varies in different countries; the international carat is 200 mg. The largest known diamond, the Cullinan, weighed 3,024 carats before cutting. The crystal of the diamond, belonging to the cubic system, is often octahedral in habit. Rhombic dodecahedral, hexakis-octahedral, and tetrahedral forms are known. X-ray examination has shown that in diamond each carbon atom is joined to four other atoms by valency bonds arranged tetrahedrally; the distance between adjacent carbon atoms is 1·54Å and the width of the hexagon rings is 2·51Å. This tetrahedral structure is the prototype of that of aliphatic organic compounds. Crystalline graphite, perfect samples of which are rare, is hexagonal. X-ray analysis shows the carbon atoms are arranged in planes, each being situated at the corner of a regular hexagon; the adjacent carbon atoms are 1·42Å apart, the rings are 2·46Å wide, and the distance between adjacent planes is 3·40Å. This structure, containing the plane hexagonal ring, is the prototype of that of aromatic compounds. So-called amorphous carbon may be graphite in an extremely fine state of sub-division; thus Warren (J. Chem. Physics, 1934, **2**, 551) has shown that single graphite layers mixed with graphite crystals exist in carbon black. In a study of the nature of industrial coke, Blayden, and Riley (J.S.C.I. 1935, **54**, 159T) survey the evidence for the existence of real amorphous carbon and give the following data relative to the ease of oxidation of various forms of carbon by potassium dichromate and phosphoric acid at 100°C.

	Mg. of CO_2 evolved in $2\frac{1}{2}$ hours from 1 g. of material.
Diamond	43
Graphite	824
Sugar charcoal	42
Electrode carbon	1,044
Wood charcoal	328
Retort carbon	258–293
Anthracite	86
Pitch coke, gas pitch	239
,, oven pitch	284
Petroleum coke	367

It is suggested that the varying reactivities, except that of wood charcoal, may be due to differences in the graphite content of the material.

It has recently been found that there are two types of diamond having different optical and photo-electric properties (Robertson, Fox, and Martin, Phil. Trans. 1934, (A), **232**, 463). The heat of combustion of diamond is 7,873 g.-cal., of graphite 7,840 g.-cal. (W. A. Roth). Diamonds occur in all shades from colourless to black, about 5% are flawless. Three varieties of diamond are used industrially; the crystal or gem variety, boart or bort, a round form with confused crystalline structure, and carbonado, or black diamond carbon, an opaque coloured aggregate of small crystals. Carbonado and bort are regarded as forms intermediate between diamond and graphite.

Many attempts have been made to prepare artificial diamonds by crystallising carbon from fused magmas—a process which may have been responsible for the natural production of diamonds. Since diamond is the hardest known substance it is a most important abrasive. It is also used for glass-cutting tools and for dies for wire-drawing. Thus tantalum, tungsten, and osmium filaments are drawn through diamond dies. Rock-drilling, cutting and polishing stones are the most important uses of bort and carbonado.

Graphite (*see* p. 313) is the most stable form of carbon at high temperatures and is very resistant to chemical action. A characteristic reaction by which it may be distinguished from diamond and charcoal is the formation of graphitic acid or oxide on treatment with nitric acid and potassium chlorate (Brodie's reagent). For this

purpose H. Moissan mixes dry graphite with strong nitric acid and then makes successive additions of dry chlorate; the oxidation must last for 12 hours and finish at 60°C., yielding a yellow solid which retains the form of the original material. Graphitic acid, C_3O, is thermally unstable and decomposes violently at 200°C., yielding carbon monoxide, carbon dioxide, and a black solid resembling graphite. Certain types of graphite need repeated treatment in order to effect complete conversion to graphitic acid. Under like conditions diamond is unaffected and charcoal is converted to a brown mass soluble in water. Graphite is slowly dissolved by a mixture of strong nitric and sulphuric acids at 300°C., and by 50% caustic potash solution at 350°C.

Certain natural and synthetic graphites when heated after moistening with nitric acid show a characteristic swelling. It has been proposed to restrict the term *graphites* to such samples, designating as *graphitites* those which do not swell under like conditions, but it is probable that the difference noted is merely due to difference in crystalline form.

The ignition temperature of graphite in oxygen is 650°–700°C., intermediate between that of diamond (800°–875°C.), and amorphous carbon (300°–500°C.). The specific heat of graphite in g.-cals. per g. is 0.152 at 0°C., 0.182 at 40°C., 0.210 at 80°C., and 0.241 at 130°C.; that of diamond is 0.104 at 0°C., 0.138 at 40°C., 0.188 at 100°C. and 0.269 at 200°C. ("Int. Crit. Tables," V, p. 94).

The manufacture of artificial graphite has been carried on since 1899 by the Acheson Graphite Company at Niagara Falls. Acheson had previously developed the manufacture of carborundum (silicon carbide) by heating coke and sand in an electric resistance furnace to a temperature of about 2,000°C.; on heating the product to a still higher temperature he found that the carbide decomposed and the silicon volatilised away leaving carbon in the form of graphite. He then developed a process in which carbon was heated in association with one or more oxides to a temperature high enough to cause a chemical reaction between the constituents and then continued heating until the combined carbon separated in the form of graphite, such elements as iron, aluminium, and silicon being removed by volatilisation. Subsequently it was found that anthracite coal could be used, the necessary metallic constituent being supplied by the ash present in the coal. Since much less than the theoretical amount of metal to form carbide with the carbon is necessary, it is supposed that the action is catalytic. In an important application of Acheson's discovery carbons for batteries, electrodes, arc lights, etc., are graphitised in order to increase their electrical conductivity. Thus petroleum coke may be moulded in admixture with tar or molasses, and silica or iron oxide; the baked product is then graphitised in the electric furnace. For use in the lubrication of machinery the finest material free from hard particles is used. For this purpose it is conveniently employed in the form of colloidal graphite, known commercially as *Aquadag* and *Oildag*, which consist of deflocculated Acheson graphite suspended in tannin and water or oil.

H. N. Kay (Oil and Colour Trades J. 1928, 73, 662) gives a survey of the varieties of graphite, their properties and uses.

Wood Charcoal is an impure form of carbon which is obtained when wood is burnt in a limited supply of air or when it is carbonised in closed vessels. It is a brittle, porous, black solid which retains the structure of the wood from which it is made and has a conchoidal fracture. Its true specific gravity varies from 1.3 to 1.9, its apparent specific gravity from 0.2 to 0.5. The heat of combustion is about 8,000 g. cal. It has remarkable properties for decolorising certain liquids and for adsorbing gases (*see* p. 315). On heating with an excess of strong sulphuric acid at 280°–300°C. charcoal yields *mellitic acid* (benzene hexa-carboxylic acid) and the anhydride of *pyromellitic acid* (benzene tetracarboxylic acid). Charcoal is more resistant than wood to influences responsible for the decay of timber and for this reason piles and stakes are often charred superficially before being driven into the ground.

The process of "coaling wood" has been carried on since very early times for the production of charcoal and its important by-products, the charcoal itself being used chiefly as a fuel and for blast-furnace work. The most primitive method involves the construction of large circular stacks of wood (the German *Meiler*); in the eighteenth century "Meiler" ovens were introduced and later brick kilns, and then iron retorts were used. Important by-products of wood carbonisation are wood tar, (Stockholm tar is made from pine wood), wood spirit containing methyl alcohol and pyroligneous acid, impure acetic acid. In spite of the recent synthetic production of methyl alcohol and acetic acid it has been found possible to operate profitably wood carbonisation with by-product recovery where a supply of wood at a sufficiently low cost is available. Frequently the by-products of wood distillation are of greater importance than the charcoal itself. Where it is intended to recover by-products deciduous wood is preferred, since it gives high yields of acetic acid and methyl alcohol; *Meiler* charcoal, however, is chiefly prepared from coniferous wood by a process of controlled burning which does not permit of adequate by-product recovery.

There are three well-marked phases in the destructive distillation of wood. First, as the temperature rises to 170°C. the distillation of water occurs, then, at temperatures up to 270°C. there occurs a preliminary decomposition resulting in the liberation of water, carbon dioxide, and carbon monoxide, and finally, at still higher temperatures, a vigorous exothermic reaction sets in, tar distils off, and carbonisation proceeds. A temperature of at least 350°C. must be reached if an odourless product is required. At 400°C. retort charcoal in a yield of about 30% by weight is obtained, having an approximate composition of C_7H_4O, and may contain about 1% of ash. *Meiler* charcoal is produced at about 500°C. and has a formula approximating to $C_{16}H_6O$; since it has greater strength and a

lower content of volatile matter it is more suitable for blast-furnace work. Such charcoals must be regarded as highly reactive forms of carbon ; thus when used as a fuel wood charcoal is noticeably more combustible than a reactive low-temperature coke. Even at ordinary temperatures retort charcoal shows a definite adsorption of oxygen from the air and this reactivity increases rapidly with a rise of temperature. It will be evident, therefore, that in preparing such material the charge must be well cooled before free access of air is permitted. It is possible that the initial adsorption of oxygen by charcoal results in the formation of a substance having the nature of a peroxide.

In constructing the *Meiler* the wood was formerly stacked in a horizontal position, but it is now usually arranged vertically. The dried wood is stacked in the form of a circular mound having an open shaft in the centre to act as a chimney ; the whole is covered with earth and small air inlets are made round the periphery. The average size of the *Meiler* used in Germany, Italy, and Sweden is about 200 cu. yds. A fire is lighted in the central air shaft and the air supply is adjusted to ensure slow combustion. In the earlier stages wood is fed on repeatedly and when the upper part of the wood is thoroughly dry, the exothermic reaction sets in, distillation begins, and the sides of the stack "sweat." In the next stage the draught holes are stopped to allow carbonisation to proceed in the presence of less air, and subsequently they are opened again. When the gases rising from the stack are no longer smoky, but clear and blue, carbonisation is completed, a process which may last 14–20 days ; the stack is then cautiously quenched. The yield of charcoal is about 26% by weight or 60% by volume of the wood used.

Charcoal kilns, formerly much used in North America, are operated in a similar way to the *Meiler*. They are brickwork chambers of beehive or rectangular shape and have a capacity of 250–400 cu. yds. Wood is fed in at the top, where the charge is then fired, draught being controlled by holes round the base which may be closed with bricks. When true carbonisation sets in the products which distil off may be led away to condensers. There are 20 or more such kilns in a battery. Where forced draught fans are used the time of carbonisation may be reduced from 3 to 2 weeks. In such ovens as the Schwartz a system of external firing is used ; wood is charged and charcoal is later discharged through doors in the side of a brickwork oven in the base of which is a fireplace, the burning gases from which pass into the charge of wood. The volatile products may be utilised for the partial recovery of by-products.

Where the process of wood carbonisation is operated for full by-product recovery, methods are used similar to those employed in the coal carbonising industries. In Sweden and Finland tube ovens are employed in which the products of combustion from the furnaces pass through tubes which are surrounded by the wood to be carbonised, but the plant most commonly used in America, Germany, France, Belgium, and Austria is a small horizontal iron retort about 3 ft. wide and 10 ft. long. The volatile products are passed through condensers to recover by-products and the gas leaving the condensers is used for heating the retort. Pairs of such retorts are arranged on either side of the furnace, and an installation may consist of 30–120 of such retorts. Stationary or movable vertical retorts are also used.

In order to reduce the cost of operating such retorts the *Carbo oven* has been introduced in Sweden. This is a large, vertical, iron cylinder having a capacity of about 500 cu. yds., the base of which is constructed of brickwork ; from the furnace at one side the heating gases pass round the outside of the retort and away to a chimney. Charging lids are fitted in the top and a discharging door at the bottom. For the purpose of minimising the labour of charging and discharging continuously-operating plants have been built, thus, in the American car retort, wood is loaded on to a waggon which is then run into a retort capable of holding 4–5 such waggons. When carbonisation is complete the charge is withdrawn and a fresh one introduced.

In certain countries where a plentiful supply of wood is available attempts are being made to utilise wood charcoal for driving motor cars. For this purpose it is burnt to producer gas in built-in producers. Rennie (Trans. Inst. Eng., Australia, 1930, 2, 101) has shown that 16 lb. of charcoal are equivalent to 1 gallon of petrol.

Animal Charcoal, or *Bone Char*, is manufactured by the carbonisation of bones in closed horizontal or vertical iron retorts. The crushed bones are treated with superheated steam or extracted with naphtha to remove fat and oil and are then placed in the retorts where they are carbonised at a red-heat, the by-products, bone oil, ammonia, and gas, being treated by methods similar to those used in gas works practice. The product, the yield of which is about 60% of the weight of the bones, is cooled in air-tight containers, crushed, and screened to the desired sizes. It should contain from 9 to 11% of carbon, the residue being tri-calcium phosphate (about 75%), calcium carbonate, magnesium phosphate, and other mineral and nitrogenous matter. The carbonaceous material may be concentrated by digestion with hydrochloric acid to dissolve out mineral matter, yielding a residue known as *Ivory Black*, which is used as a pigment or for the purification of fine chemicals or wines when the use of ordinary bone black is inadmissible. The most important industrial application of animal charcoal is for the refining and decolorisation of sugar, a practice which was introduced by Derosne in 1812 (*see* Charcoal, active, p. 315). Horton (Ind. Eng. Chem. 1923, 15, 519) suggests that bone char owes its power of removing colour to the presence of active carbon and that the nitrogenous organic matter present serves as a reserve to supply fresh carbon on ignition. In practice it is customary when the adsorptive capacity shows an appreciable decrease to submit the charcoal to a process of regeneration, usually heating to redness, so that it is possible to use it for as long as 2 years, after which it is used as a pigment or a fertiliser. Results of comparative studies of bone char and the newer

carbons are described in the Annual Reports of the Society of Chemical Industry (1924, 9, 463; 1925, 10, 469; 1927, 12, 503).

Lampblack or Soot is prepared by burning oil, tar or resin in a limited supply of air. It has been manufactured for very many years in Egypt and China, being valued for its intense black colour. A special variety of lampblack known as carbon black (*see below*) is formed when gas burning in insufficient air impinges on a metal or stone plate, there being a striking improvement in colour and tinctorial strength. Both of these products consist essentially of carbon and the difference in their nature is not clearly understood; for industrial purposes their value is assessed by empirical tests.

Early methods of making lampblack were extraordinarily crude. Heated resin was ignited and the products led into tents lined with sheepskin, from which the deposited black was collected periodically. Later improved methods were developed in which smoke generated in a furnace was passed into a tower with a conical roof, through the top of which the waste gases escaped.

In modern procedure tar oils, particularly creosote oil or petroleum oils, are burnt in a brick or stone furnace. Air is admitted in carefully regulated amounts and the oil is vaporised by feeding it on to heated plates. From the furnace the smoke is passed into a series of chambers in which baffles are built. Periodically the chambers are allowed to cool down so that the product may be removed, care being needed as the lampblack is pyrophoric.

Lampblack has for long been the basis of ink pigments, but for printing inks it has been largely displaced by carbon black. Both products are used for black paint pigments.

Thermatomic Black is obtained by the thermal decomposition of hydrocarbons. A. W. Francis (Ind. Eng. Chem. 1931, 23, 612) states that yields as high as 30–40% may be obtained, but that the product is inferior in tinctorial power and unfit for use as printers' ink. It finds limited use in rubber compounding, chiefly in the side walls of tyres.

Carbon Black, or Gas Black, was first used chiefly in place of lampblack for printing inks, but when, during the Great War, difficulties were experienced in the United States in obtaining zinc oxide as a filler for rubber, it was found by the B. F. Goodrich Co. that carbon black had valuable qualities for improving the mechanical properties of rubber. It may be noted that this property had already been revealed in English patents. The American industry developed so rapidly that, according to statistics issued by the U.S. Bureau of Mines, the production in 1935 amounted to 352,740,000 lb. The Panhandle district of North Texas was responsible for 75% of this production, and 90% of it was used for the reinforcement of rubber. It is estimated that this production of black involved the burning of 229×10^9 cu. ft. of natural gas. The consumption of natural gas for this purpose is limited to locations where it cannot be disposed of more profitably as a fuel. Owing to the low cost of production and the high quality of the product, the industry became virtually an American monopoly, the chief importers being the United Kingdom, France, Germany, and Canada.

It is customary before burning the gas for the production of black to treat it for the recovery of gasoline. Of the black made in America 80–90% is produced by the channel process, which, whilst admittedly extravagant in respect of the amount of gas used, gives a product superior to that produced by other processes. The plant is housed in long, low buildings from 100 to 150 ft. long, 10 ft. wide, and 9–10 ft. high. A factory may consist of from 20 to 70 of such hot houses. Inside each house is a series of iron channels 6–8 ft. wide, about 100 ft. long, and about 6 ft. from the ground; these channels move slowly backwards and forwards whilst the flames of the burning gas impinge on them from a row of burners below. The deposited black is removed mechanically by means of iron scrapers and falls into hoppers below, from which it passes into spiral conveyors. The channels are suspended from trucks running backwards and forwards on overhead rails. Slide doors in the bottom of the house permit control of the air admitted for combustion and ventilators in the roof facilitate draught control and escape of the waste products of combustion. The collected black is carefully screened to remove grit and coarse material before packing. The average yield by this process is 1 lb. per 1,000 cu. ft. of gas, the product being very glossy and of intense colour.

In another process gas is burnt in a series of soap stone burners and the flame impinges on a small rotating iron disc of about 3 ft. diameter. Carbon is scraped off continuously and falls into a hopper below.

Neal and Perrott (U.S. Bureau of Mines, Bull. 1922, p. 192; J.S.C.I. 1922, 41, 770A) survey the manufacture, properties and uses of carbon black, giving analyses of blacks of proprietary makes and a bibliography of patent and technical literature. Dawson and Hartshorn (Trans. Inst. Rubber Ind. 1930, 5, 48) have made a chemical, physical, and mechanical examination of lampblack, carbon black, and acetylene black (made by the explosive combustion of purified acetylene in closed chambers). As shown below, lampblack is the least pure form of carbon:

	Sp. gr.	% of carbon
Acetylene black . . .	1·89	99·6
Gas black .	1·77	97·4–99·0
Lampblack . . .	1·78	91·4–96·1

Gas black has a particle size of 0·1–0·2μ, lampblack is coarser and has inferior reinforcing qualities. Drogin (India Rubber J., 1935, 90, 259) describes methods for manufacturing carbon black. The natural gas should preferably be low in nitrogen content and relatively free from hydrogen sulphide. Gasoline recovery is desirable for economic reasons and for the production of a more uniform gas. In the channel process the construction of the special talc burner tips has an important influence on the quality and yield of black.

There is some production of carbon black in Russia and production was started in Formosa by the Japan Petroleum Co. in 1931. In

Belgium "carbonalpha" is made from carbon monoxide, which is decomposed catalytically to carbon and carbon dioxide (Chem. Trade J. 1936, **99**, 153). Strenuous efforts in Germany have resulted in commercial production of a black equal in quality to the American product, but considerably higher in price. In B.P. 450876 of 1935 the I.G. Farbenindustrie A.-G. protects the production of carbon black by the catalytic dehydrogenation of hydrocarbons such as benzene and naphthalene. Dittrich (Brennstoff-Chem. 1935, **16**, 121) surveys the production, properties, and testing of various blacks with particular reference to German development work; he includes a bibliography. Reviews of more important recent developments in the manufacture of carbon black and of studies of its use as a compounding ingredient for reinforcing rubber will be found in recent issues of the "Annual Reports of the Society of Chemical Industry."

It is customary to compress carbon black before sale so that 22–24 lb. are contained in a cubic foot instead of 10–13 lb. in the uncompressed state. To reduce the dustiness of the product it may be prepared in a special granular form.

Amounts up to 40% are added to rubber for mechanical reinforcement. Whereas the tensile strength of a rubber-sulphur mixture is 1,150 lb., the addition of 35% of black increases it to 4,000 lb.

Recent work has led to the introduction of black of higher colour intensity which is finding wider applications in paints, plastics, and films. The production of these improved products involves the use of special burning conditions, and as the yield is much lower the products are more expensive, but at the same time the durability of the paint film is favourably affected. The following British Standard Specifications have been issued for varieties of carbon used as paints:

1927	284	Carbon black.
,,	285	Bone black.
,,	286	Vegetable black.
,,	287	Lampblack.
,,	288	Mineral black.

Revisions are in course of preparation.

The carbon electrode was first employed by Sir Humphry Davy, who used two rods of carbonised wood to produce an electric arc. Later, in 1844, Foucault used for the same purpose rods sawn from retort carbon, the dense carbonaceous mass which gradually accumulates in coal gas retorts. Staite and Edwards in 1846 patented the use of sugar as a binding agent for coke, the moulded mixture being cemented together by baking, and this is in essence the principle which is now employed for manufacturing purposes. The process acquired technical importance for the manufacture of carbons for arc-lighting, and later of electrodes for electric furnaces, and for the preparation of aluminium, magnesium, caustic and alkali, chlorine, etc., as well as of calcium carbide, graphite, carborundum, carbon disulphide, cyanamide, etc. Mantell ("Industrial Carbon." Chapman & Hall, Ltd., London. 1928) gives the total annual value of furnace electrodes in America at over $10,000,000, next in importance being Germany, the United Kingdom, and France; he describes an electrode made by the National Carbon Co. of America which was 9 ft. long, 40 in. in diameter, and weighed 8,000 lb.

As has been indicated above, the essential principle of electrode manufacture is admixture of the basic material with the binding agent, moulding, and baking. The basic material is usually either coal or coke. Bituminous coal is little used owing to its high content of volatile matter and ash, but anthracite is used extensively. Gas coke may be used where contamination of the product is unimportant, *e.g.* in the production of calcium carbide, but for the purest carbons it is customary to use petroleum coke or pitch coke. The former product is obtained in the intermittent process of petroleum distillation, the latter by the carbonisation of pitch. Retort carbon is used more particularly for making carbon brushes. The binding materials most frequently used now are coal tar, water gas tar, and pitch. Tars are largely used in making moulded electrodes, whereas pitch is used in the extrusion process. Before mixing in the binder it is necessary to calcine the basic material to expel volatile matter, which is effected by heating in an electric furnace or a gas-heated oven of the continuous vertical retort type. The product is submitted to a process of grinding to produce a suitably graded material, which is then mixed with the necessary quantity of binder. The electrode is shaped, either by high compression in a mould or by forcing the mixture under hydraulic pressure through a die—the so-called extrusion process. The product is then baked to a temperature of about 1,000°C. to decompose the binding material and finally the article is cleaned and tested to determine the electrical resistance.

Graphite electrodes are prepared by submitting ordinary electrodes to the Acheson graphitisation process in an electric furnace. As their electrical resistance is about one-fourth that of ordinary electrodes, they are used in processes where low resistance is essential, for example, in the electrolytic production of chlorine and caustic soda. Carbon brushes and arc-light carbons are made by methods essentially the same as that employed for electrodes. In the Söderberg continuous system the electrode is prepared in the furnace in which it is subsequently used by forcing into the upper part of the furnace an unbaked mixture of carbon and tar. Baking of the electrode occurs as it passes down into the furnace. R. C.

GRAPHITE.

A form of carbon crystallised in the rhombohedral system, known also as *plumbago*, and popularly as *black-lead*. It occurs usually as compact and crystalline masses, but occasionally as six-sided tabular or scaly crystals which cleave into flexible laminæ parallel to the basal plane. It is iron-black or steel-grey in colour, with metallic lustre, and has a sp.gr. of 2·25. In consequence of its softness (H.=1) and the ease with which it produces a black streak

when rubbed on paper, it is largely used in the manufacture of pencils whence the name "graphite" given to it by Werner, from γράφω (I write). It was formerly called *molybdæna*, and confused with molybdenite (MoS_2), a mineral which also gives a black mark on paper. (On the history of these names, and of plumbago, v. J. W. Evans, Trans. Philological Soc. 1908, 133.) Graphite seems to have been first recognised as a distinct mineral by Gessner, who figured a lead pencil in 1565 (Roscoe) Scheele in 1779 showed that graphite was a kind of mineral carbon, since it could be converted into carbon dioxide by the action of nitric acid As the carbon is usually associated with more or less iron, the older mineralogists described the mineral as a "carburet of iron," but Vanuxem demonstrated that the iron is present as ferric oxide and not as a carbide The ash left on the combustion of graphite usually contains, in addition to the ferric oxide, silica, alumina, and lime

Exposed on platinum foil to the flame of the blowpipe, graphite burns, but often with more difficulty than diamond. When heated with a mixture of potassium dichromate and sulphuric acid, it disappears. In order to obtain perfectly pure graphite, the mineral is first ground and washed to remove earthy matter, and then treated, according to *Brodie's method*, with potassium chlorate and sulphuric acid ; on subjecting the resulting product to a red heat pure carbon is obtained in a remarkably fine state of division.

The following analyses are selected from a large number by C. Mène (Compt. rend. 1867, 64, 1091) :

—	I	II.	III.	IV
Carbon .	91 55	81 08	79 40	78 48
Volatile matters .	1 10	7 30	5 10	1·82
Ash . . .	7 35	11·62	15 50	19 70
	100 00	100 00	100 00	100 00
Sp gr. .	2 345	2·303	2 350	2 286

I. Very fine Cumberland graphite. II. Graphite from Passau, Bavaria. III. Crystallised graphite from Ceylon. IV. Graphite from Buckingham, Quebec.

Graphite when used for pencils is frequently mixed, in a powdered state, with pure clay, and the mixture consolidated by hydraulic pressure. It is also sometimes mixed with sulphur or with antimony sulphide. The finest pencil lead was yielded by the ancient mine at Borrowdale in Cumberland, where it occurred in pipes, strings and irregular masses or "sops," associated with a dyke of diorite and with intrusive masses of diabase, in the Cambro-Silurian volcanic series known as "the green slates and porphyries." The Cumberland graphite was formerly termed "wad," a name sometimes applied also to native oxide of manganese. (For description of the old Borrowdale workings v. J. C. Ward in Mem. Geol. Survey on Lake District, 1876.) A small amount of graphite has been obtained from the Craigman mine, near Cumnock in Ayrshire ; here the mineral usually exhibits a columnar structure, and has been produced by the baking action of dykes of igneous rock on seams of coal (v. Special Reports on the Mineral Resources of Great Britain, Mem. Geol Survey, vol. v, 2nd ed., 1917).

Excellent graphite is found in Siberia, especially at the Mariinoskoi mine, in the Tunkinsk Mountains, Irkutsk. This deposit, discovered in 1838, occurs in gneiss, associated with diorite ; it has been largely worked by M. Alibert to supply Faber's pencil factory. In 1860 graphite was discovered in granite near the Lower Tungusska river, and workings were undertaken by M Siderov. (For Russian graphite v N Koksharov, Materialien z. Mineralogie Russlands, 1862, 4, 153, where analyses are given)

The best quality of flake graphite found in large quantities is that from Ceylon The mineral is widely distributed through the western and north western provinces of the island, and is obtained from a large number of small pits, there being but few mines of any size. The output is variable—10,000–30,000 tons per annum , in 1916 it was 33,400 tons, valued at £1,500,000. (On the graphite deposits of Ceylon, v A K Coomara Swámy, Mineralogical Survey of Ceylon, 1903, etc ; Quart J. Geol Soc 1900, 56, 590.) In India, graphite is found at several localities, chiefly in the Madras Presidency, the best coming from Travancore, but even this is inferior to that from Ceylon.

In the United States, graphite is widely distributed, but rarely in sufficient quantity to be worked The principal locality is Ticonderoga, in Essex Co, New York, where the Dixon Crucible Co. have worked a schist containing about 10% of graphite. It has also been worked to a limited extent near Raleigh, North Carolina ; at Stourbridge, Mass. ; at Cumberland Hill in Rhode Island ; and at Sonora in California. The graphite "ores" are crushed or stamped, and then washed, whereby the flakes of graphite are readily separated from the denser matrix. In the Laurentian gneiss of Canada, graphite is of frequent occurrence, and is worked at some places, as at the Buckingham mines, Ottawa Co., Quebec. The mineral is usually found in veins and nodular masses, or finely disseminated through bands of limestone It is widely distributed in the gneissic rocks of Madagascar, and is there mined at a number of localities, with an output of 10,000–30,000 tons per annum. Graphite is also extensively mined at several places in Korea, where the deposits have the form of beds, nests, stocks, and veins in gneiss and metamorphosed Palæozoic sediments.

In Europe, extensive deposits of graphitic schists occur in the Eastern Alps and in the mountainous region (Bohmerwald) between Bohemia and Bavaria. These are extensively mined in Bohemia, Moravia, Lower Austria, and Styria, where the annual output has reached 50,000 tons ; but the material is amorphous and of inferior quality, containing often 50% of ash Considerable amounts are also obtained at the well known locality at Passau in Bavaria and

in the north of Italy. (On Alpine Occurrences of Graphite *v.* E. Weinschenk, Abhandl. bayer. Akad. Wiss. 1898, **19**, 509, 521; 1901, **21**, 279.)

Daubrée obtained graphite artificially by decomposing carbon disulphide in contact with metallic iron at a high temperature; while H. Sainte-Claire Deville prepared it by passing carbon tetrachloride vapour over fused cast iron. Crystalline graphite is often formed in blast-furnace slag during iron smelting, and is known to workmen as *kish*; and it is present in grey pig iron. Considerable quantities of graphite are now produced commercially, together with carborundum, in the electric furnace (*see* p. 310). The artificial production of graphite (as well as various properties of the natural mineral) is dealt with by H. Moissan ("The Electric Furnace," London, 1904). Graphite also occurs in certain meteoric irons, such as that of Toluca in Mexico. A cubic form of graphite carbon, discovered in a meteoric iron from Youndegin, Western Australia, has been described by Fletcher under the name of *Cliftonite* (Min. Mag. 1887, **7**, 121).

In consequence of its refractory character, graphite is largely used in the manufacture of crucibles, retorts, twyers, and other objects required to withstand high temperatures. For crucibles, the powdered mineral is mixed with Stourbridge fireclay, and made into a paste with water; the kneaded mass is allowed to lie for many weeks before the crucible is moulded; the vessel when moulded is slowly dried, and carefully fired in a saggar.

As a lubricating agent graphite is highly valued, since it diminishes friction and tends to keep the moving surfaces cool. To obtain the best results the powdered mineral should be carefully selected and sized. For steam cylinders it is used dry; for heavy bearings it is mixed with grease; and for light bearings with oil. Made into a paint with linseed oil, it has been advantageously employed as a coating for metal work. Graphite is also used dry for polishing stoves and other objects of cast iron, the thin flakes forming a lustrous coating which protects the metal. Blasting powder and heavy ordnance powders are likewise glazed with graphite, for though it slightly diminishes the explosive force of the powder it protects it from damp. Being a good conductor of electricity, graphite is used in electrotyping, as originally suggested by Murray; the moulds upon which the metal is to be deposited receiving a conducting surface by being coated with finely divided graphite.

For the method of rapidly analysing graphite in use at the Pittsburgh Laboratory of the U.S. Bureau of Mines, *see* U.S. Bur. Mines, Bull. 1920, **112**, 43; J.S.C.I. 1921, **40**, 79, A.

E. Donath, "Der Graphit, eine chemisch-technische Monographie," Leipzig and Wien, 1904; Graphite, Imp. Mineral Resources Bureau, London, 1923; H. S. Spence, Graphite, Dept. of Mines, Ottawa, 1920, Publ. No. 511; A. Haenig, "Der Graphit, eine technische Monographie," Wien and Leipzig, 1910; O. Stutzer, "Die wichtigsten Lagerstätten der 'Nicht-Erze,'" 2nd ed., vol. 5, Berlin, 1933.

L. J. S.

CHARCOAL, ACTIVE.

The name *active charcoal*, or *active carbon* which is often used, is applied to a heterogeneous group of products consisting essentially of amorphous carbon with varying amounts of ash and possessing in an enhanced degree the adsorbent properties of wood and animal charcoals (*q.v.*). These products were unknown before the War and owe their existence mainly to the efforts then made to produce an efficient adsorbent for toxic gases at a sufficiently low cost. A few special decolourising carbons, however, were marketed prior to 1914. Consequent on war-time experience many new uses have been found for active charcoal and at the present time it is a material of considerable industrial importance and the subject of numerous patents.

Various industrial carbons are now on the market under different trade names. These are either in the form of extruded pellets or of granules or fine powders. They may conveniently be divided into two types: (1) the gas-activated type, (2) the chemically activated type. The two types differ in the general form of the adsorption isothermal, *i.e.* in the particular way in which activity varies with sorbate concentration or partial pressure. Gas-activated charcoals are particularly efficient at low-pressures while chemically activated charcoals, in general, are not so efficient. Care must be taken to select the right type of charcoal for the operation in view.

Manufacture.—Any carbonaceous material which yields a coke on being heated or otherwise carbonised, *e.g.* wood, coal, nutshell, peat, sugar, can be used as source of active charcoal, but the raw materials most commonly employed in its manufacture are peat, wood, and coal (O. Kausch, "Die aktive Kohle," 1928, Ergänz-Band, 1932, Wilhelm Knapp, Halle, a.S.). The procedure varies considerably according to the process adopted, but it involves at some stage or other (*a*) the production of porous, amorphous carbon, (*b*) the activation or surface cleaning of this carbon. Manufacturing processes fall under three headings: (1) direct processes, (2) briquetting processes, (3) chemical processes. It should be noted that direct processes as used during the War have now been to some extent overshadowed by chemical and briquetting processes, but a description of them is included since they might assume a greater importance if and when occasion arises.

(1) *Direct Processes.*—Two separate operations are involved: (i) the carbonisation of the raw materials in carbonising plant, (ii) the activation of the resulting charcoal in similar or special plant. In this country the raw materials (birchwood chips, nutshell, or vegetable ivory) were carbonised for 2–6 hours at 1,000°C. in horizontal or inclined gas retorts and the resulting charcoal extracted and quenched. It was then crushed and screened to $\frac{1}{8}$-in. particles, charged into a second retort, and either (*a*) heated in the closed retort for 10–20 hours at 1,000°C. in presence of steam and air or (*b*) heated in a current of steam for 3–10 hours at 1,000°C. Moderately active charcoals were obtained in yields of 10–14% of the raw material

used. In America, fruit stones, nutshell or anthracite coal were used and the procedure differed somewhat in the activation stage (Dorsey, Ind. Eng. Chem. 1919, 11, 281; Lamb, Wilson, and Chaney, *ibid.* 420). Two methods of activation were used. In the first method the crushed, unactivated material was passed continuously through a special vertical activating chamber. This consisted of a 7 in. nichrome reaction tube surrounded by an outer retort in which gas was burnt, and having a perforated nichrome steam tube along its centre line. The charcoal was heated to 800°–1,000°C. by the combustion of gas in the outer retort, while superheated steam was admitted to the heated central column. In the second method ("Static" activation) the crushed, carbonised material was packed into shallow, refractory trays arranged in banks on a steel truck which was wheeled into an internally gas-fired kiln. This was then sealed and the charcoal heated to 850°C. for 4 hours, water being continuously admitted at a cool part of the kiln. A higher yield and more uniform product was obtained by this method.

Recently the direct method of manufacturing active charcoal from coal in gas-making plant has been re-investigated (Communication from the Fuel Research Station, J.S.C.I. 1936, 55, 223T). According to this communication it is essential (*a*) to use a non-swelling coal, (*b*) to carbonise at temperatures between 450° and 500°C., and (*c*) to activate with steam at 950°C. The coal is crushed and screened to 1–⅜ in. pieces which yield a coke of suitable size for activation. Unless low temperature retorts are available special arrangements require to be made to keep the carbonisation temperature at the desired level. Activation is carried out in continuous vertical retorts one of which may be made to serve as a superheater for the steam. The most active product is obtained by steaming the coke at 950°C. until 75% of it has been gasified, which requires 200–300% of steam. With a suitable coal highly active products can be obtained in yields of about 12½% of the lump coal taken.

The importance of a low carbonisation temperature in the case of coals was first pointed out by Lamb, Wilson and Chaney (*l.c.*) and Chaney has since placed this temperature at 600°C. (U.S.P. 1499908). It appears that at high temperatures the carbon is graphitised and does not then readily react with steam. Probably for this reason high temperature gas cokes cannot be activated to any useful extent. According to Lamb, Wilson and Chaney activity is due simply to the increase in porosity and internal surface brought about by the activating gas. Hydrocarbons produced during carbonisation and strongly adsorbed by the carbon atoms are burnt away in activation so that the adsorptive forces are released. Much external combustion occurs at the same time, however, which explains in part the low yields obtained in direct processes.

The use of steam for activation was first investigated by R. Ostrejko in Austria (G.P. 136792, 1916) and independently by N. K. Chaney in America (U.S.P. 1497543). It is ineffective below 800°C. and is commonly employed at temperatures between 850° and 950°C. Air is effective at temperatures as low as 350°C., but since the reaction is exothermic control is more difficult and in addition the products are more friable than those obtained with steam. Air is now rarely used alone. Mixtures of steam and air and of steam and carbon dioxide are mentioned in the literature. According to B.P. 357778, 1930, the addition of 6% of oxygen to steam reduces the activation temperature to 500°–600°C. which is maintained by the heat of reaction. Sulphur vapour is mentioned as an activator in B.P. 224521, 1924; 270505, 1926.

(2) *Briquetting Processes.*—Few raw materials have the necessary density and structure for direct conversion into active charcoal. Generally the products are friable and the yields low. As mentioned above only one class of coal is suitable for use in the direct process. The employment of briquetting in manufacture greatly widens the choice of raw materials and at the same time increases the yield and hardness of the products obtained therefrom. The raw materials may be briquetted under pressure and then carbonised and activated; more often they are first carbonised and finely ground after which they are agglomerated with a binder such as tar, pitch, petroleum oils, etc., subdivided, recarbonised, and finally activated. Different raw materials or cokes may be blended by this method. Bituminous and anthracitic coals, carbon black, petroleum coke, etc., may be converted by this method into satisfactory charcoals with yields up to 25% of the raw material taken (U.S. Bur. Mines, Bull. Tech. Papers No. 479, 1930).

The well known product *Norit* is a steam activated, briquetted charcoal (B.P. 199323 and 206862, 1923; 228954 and 247241, 1924). Beechwood charcoal is pulverised and incorporated with an equal weight of wood tar and 1% $NaOH$, the mixture then being compressed under high pressure into pellets. These are packed into wire shelves on a truck which is wheeled into a kiln heated by waste gases to 100°C. After a sufficient time the hardened pellets are withdrawn and blown into an elevated hopper from which they pass into two rotary kilns in series, the upper one at 160°C. and the lower one at 550°C. The lower kiln is internally fired, the waste gases serving to heat the upper one. The carbonised pellets pass from the lower kiln into a third rotary kiln for activation with superheated steam at 800°–1,000°C. This kiln is lined with refractory material and internally fired. It is only slightly inclined, and revolves slowly so that the charcoal is retained several hours. It is then cooled out of contact with air.

(3) *Chemical Processes.*—The impregnation of carbonaceous materials with compounds such as the chlorides of zinc, calcium, magnesium, etc., alkalis, sulphuric and phosphoric acids, affords a means of producing high yields of charcoal at relatively low temperatures which requires but little subsequent activation. The action of the reagents appears to be one of dehydration with direct liberation of carbo

unaccompanied by the tarry materials of pyrogenation (Urbain, "Recherches et Inventions," 1926, No. 130). Manufacturing processes based on this method of carbonisation involve grinding of raw materials and extrusion under pressure of the pastes formed with the reagents so that the advantages of briquetting already mentioned are thereby included. The products are known as chemically activated charcoals and are of a special type. The process of chemical activation as now commonly practised is due to R. Ostrejko (B.P. 14224, 1900), who sought to produce a highly active decolorising charcoal.

The French product known as *Urbain Charcoal* is an example of this class. In manufacture (Urbain, *op. cit.*, p. 80) peat of low ash content is finely ground, mixed with phosphoric acid and allowed to stand some time. The paste is then forced into threads under pressure which are dried with waste gases in a rotary kiln and broken into short lengths, after which they are heated in gas retorts at about 1,000°C. for 8–10 hours. In this process the phosphoric acid present is reduced to elementary phosphorus which passes as vapour to a combustion chamber where it is burnt and reconverted to phosphoric acid. The charcoal is cooled, thoroughly washed with hydrochloric acid and water, and finally dried at 300°C. Although a high temperature is employed in the process no steam is required, activation resulting from the reduction of phosphoric acid which occurs uniformly throughout the mass of material.

The charcoal made by the Bayer process of the I.G. Farbenindustrie A.-G. (B.P. 10126, 1914; G.P. 290656, 1914; 310092, 1916) is a chemically activated charcoal. Selected peat is finely ground and agglomerated with 50% zinc chloride solution and extruded under pressure through plates perforated with $\frac{1}{8}$-in. holes. The extruded material then passes through an inclined, rotary kiln heated internally by the products of combustion of gas burned in a furnace at the lower end. In carbonisation the material reaches a temperature of about 650°C., after which it is received in iron boxes and cooled out of contact with air. It is then subjected to counter-current washing with dilute hydrochloric acid to remove zinc compounds, and finally washed with water in wooden vats, after which it is dried in kilns in an air stream heated to 275°C. The final stage consists in mechanical screening to remove smalls and dust.

Properties and Uses.—The outstanding property of active charcoals is their *adsorptive activity* towards vapours, gases, and dissolved substances. Hardly less remarkable is their *versatility* as adsorbents—a fact first demonstrated by Hunter (J.C.S. 1865, 18, 285). Activity is expressed in terms of adsorptive capacity which is measured for any given substance by the quantity adsorbed under specified conditions of temperature and pressure. According to Lamb, Wilson, and Chaney (*l.c.*) active charcoals as now made have 50–200 times the adsorptive capacity of the older wood and animal charcoals. All known gases are adsorbed to a greater or lesser extent although in the case of certain of them adsorbability is only slight. Helium is the least adsorbable. At 0°C. and 760 mm. coco-nut charcoal only adsorbs twice its volume of this gas. Then follow in order of increasing adsorbability hydrogen, argon, nitrogen, oxygen, and carbon monoxide, 21 vols. of the latter being adsorbed (Dewar, Compt. rend. 1904, **139**, 261). Later work has shown that when oxygen is adsorbed by highly evacuated charcoal a fraction of it is retained and can only be recovered at higher temperatures in the form of oxides of carbon. The surface layer of oxygen appears to enter into chemical combination with the carbon atoms—a view supported by the exceedingly high initial heat of adsorption of oxygen (Rhead and Wheeler, J.C.S. 1913, **103**, 461; Lowry and Hulett, J. Amer. Chem. Soc. 1920, **42**, 1393). In general, the adsorbability of gases on charcoal follows the order of condensability. Coco-nut charcoal adsorbs about 200 times its own volume of ammonia at N.T.P. Most known vapours are strongly adsorbed by active charcoal. The following data for some common substances serve to show the order of activity of coco-nut charcoal towards inorganic and organic vapours. The data were obtained at saturation pressure and at 0°C. CCl_4=71·0%; CS_2=58·1%; C_6H_6=41·9%; $(C_2H_5)_2O$=36·2% (Coolidge, J. Amer. Chem. Soc. 1924, **46**, 596). Water vapour is exceptional, being adsorbed in only small amounts below 8–10 mm. partial pressure (Berl and Andress, Z. angew. Chem. 1921, **34**, 369; Allmand and Hand, J. Physical Chem. 1929, **33**, 1161). Hydrocyanic acid is also exceptional, being but slightly adsorbed at low pressures. Studying a group of charcoals Allmand and Chaplin found a maximum adsorbability of about $\frac{1}{2}$% at 0·2 mm. and 25°C. (Proc. Roy. Soc. 1931, A, **132**, 460). In general, the higher the molecular weight of a compound the greater will be its adsorbability, but quantitative relationships exist only in the case of organic compounds of the same class.

Adsorptive capacity increases with pressure and decreases with temperature for all substances, the pressure/quantity relationship at constant temperature being given by the adsorption isothermal, and the pressure/temperature relationship by the isostere. Numerous data showing these relationships for various substances and different charcoals have been collected by McBain ("The Sorption of Gases and Vapours by Solids," p. 58, Routledge, London, 1932), and a review of adsorption equations has been made by Swan and Urquhart (J. Physical Chem. 1927, **31**, 251). A well-known equation relating quantity adsorbed (x/m) and pressure (p) or concentration (c) is: $x/m=kp^{\frac{1}{n}}$ or $kc^{\frac{1}{n}}$, where x is the quantity of substance adsorbed by m of charcoal and k and n are constants characteristic of substance and temperature. This is often referred to as the classical or "exponential" equation, and has a wider applicability than most of them. No single equation, however, applies accurately over the whole known pressure range (*v.* Adsorption).

The rate of development of pressure, measured by dp/dq on the isothermal, is initially very

low in the case of vapours, so that considerable quantities are adsorbed at what might appear zero pressure. A definite relationship between quantity and pressure obtains, however, down to the lowest concentrations of adsorbed vapour (Allmand and Chaplin, Proc. Roy. Soc. 1930, A, 129, 250). In the low-pressure region charcoals differ markedly in activity. Allmand and Chaplin found that at 0·01 mm. and 25° a chemically activated charcoal adsorbed 4·7% of CCl_4, while a steam-activated coconut charcoal adsorbed 16·5%. The activity in this region bears no relation to that at higher pressures, so that tests made at fixed pressures have a limited significance (Allmand and Manning, J.S.C.I. 1928, 47, 369T). Vapour adsorbed at pressures represented by the steep part of the isotherm is easily removable from the charcoal, but that adsorbed prior to this is not. A measure of the retentive power is known as the *retentivity* of charcoal, which is usually determined for any given vapour by streaming dry air or nitrogen through the charged charcoal at 25°, 100°, or 130°C. until the rate of loss becomes insignificant. So far retentivity has not been very rigidly defined. According to Chaney, Ray and St. John (Ind. Eng. Chem. 1923, 15, 1252), the retentivity of charcoal for vapours is proportional to its adsorptive capacity for non condensable gases and to its decolorising power for liquids, these properties all being manifestations of *adsorption* on active surface (chemical forces) as distinct from condensation in capillaries (physical forces). Macy finds retentivity for vapours to be proportional to the heat of wetting and proposes the latter as a basis of test for the activity of charcoal (J. Physical Chem. 1931, 35, 1397).

Steam-activated nut and briquetted charcoals in general have a high retentivity. Some exhibit up to one third of their total capacity below a pressure of 0·1 mm. Chemically activated charcoals, on the other hand, have low retentivity but high capacity for vapours at moderate partial pressures.

The process of adsorption by active charcoal is accompanied by the evolution of heat as first shown by Favre (Ann. Chim. Phys. 1874, [v], 1, 209). The quantity of heat per unit mass of charcoal is a maximum in the initial adsorption stage, where it greatly exceeds the latent heat of vaporisation. It declines with increasing adsorption and finally tends towards a constant value considerably higher than the latent heat of vaporisation (Titoff, Z. physikal. Chem. 1910, 74, 641 ; Keyes and Marshall, J. Amer. Chem. Soc. 1927, 49, 156). Water is exceptional, and exhibits throughout a heat of adsorption differing but slightly from the latent heat of vaporisation (Coolidge, J. Amer. Chem. Soc. 1927, 49, 708). According to Lamb and Coolidge (*ibid.* 1920, 42, 1146), the integral heat of adsorption h may be calculated from the quantity of vapour x adsorbed by active charcoal from the equation $h=mx^n$, in which m and n are constants characteristic of the vapour. Heats of adsorption in g.-cals./mol. for some common vapours measured at about half their saturation values on charcoal at 0° are as follows : CS_2=12,500 ; $CH_3{\cdot}OH$ =13,100 ; $CHCl_3$=14,500 ; C_6H_6=14,700 ; $C_2H_5{\cdot}OH$=15,000 ; $(C_2H_5)_2O$=15,000 (Lamb and Coolidge, *l.c.*). Oxygen is unique in exhibiting initial heats of adsorption far in excess of those for other substances, which tends to confirm the previous evidence for combination with carbon prior to adsorption proper. Initial heats of adsorption for oxygen as high as 72,000 g.-cals./mol. have been observed by Keyes and Marshall (*l.c.*).

Active charcoal has been observed to undergo a slight expansion during the adsorption of CO_2, NH_3, SO_2, H_2O, C_6H_6, and C_5H_5N. The phenomenon is probably a general one. The expansion is a function of the quantity adsorbed, is reversible, and the upper limit is of the order of ½% by volume of charcoal (Meehan, Proc. Roy. Soc. 1927, A, 115, 199 ; Bangham *et al.*, *ibid.* 1930, A, 130, 81 ; 1932, A, 138, 162).

The velocity of adsorption as measured *in vacuo* is very high for all but the final stages of adsorption. From a practical point of view it is instantaneous (Dewar, Proc. Roy. Inst. 1937, 18, 750). In adsorption from the gaseous phase the presence of inert gases causes but slight impedance provided there is efficient contact between gas and charcoal, *e.g.* with a time of contact of only 0·03 second, coconut charcoal in 10 mesh granules very efficiently adsorbs chloropicrin from air in a stream containing 7,000 p.p.m. (Lamb, Wilson and Chaney, *l.c.*) At higher vapour concentrations such as are often found in industrial gases, times of contact of several seconds are allowed to facilitate dissipation of the heat of adsorption and so avoid unduly raising the temperature of the charcoal. The velocity of adsorption from solution is low in comparison with that observed in the gaseous phase, being dependent on the rate of liquid diffusion. In general, times of contact 50-100 times as long as those for adsorption from the gaseous phase have to be employed, and liquids for treatment are either filtered at low rates through beds of active charcoal or heated and agitated for definite times with a sufficient quantity of the adsorbent in a finely divided state.

The *true density of active charcoal* is the density of the solid carbon wall and lies between 2·2 and 2·3 g./c.c. This is sensibly equal to that of graphite (2·26 g./c.c.). The *bulk density* is the weight of 1 c.c. of dry granules or powder, and varies considerably with the source and mode of manufacture of the active charcoal, and to some extent with grain size and shape. Industrial charcoals for the treatment of gases are usually in the form of spheroidal or cylindrical particles of $\frac{1}{16}$ to $\frac{1}{4}$ in. diameter, while those for the treatment of liquids are in the form of fine powders. The bulk density of chemically activated charcoals commonly lies between 0·20 and 0·40 g./c.c., while that for steam-activated nut- and briquetted-charcoals lies between 0·40 and 0·55 g./c.c. It is determined by weighing 100 c.c. of active charcoal in a cylinder of not less than 5 cm. diameter and making a correction for moisture present.

The *specific heat* of active charcoal corresponds with that of graphite (*q.v.*) and thus changes materially with temperature.

The utility of active charcoal for the

production of high vacua was first pointed out by Sir J. Dewar (B.P. 13638, 1904) who observed the great increase in adsorptive capacity which resulted from cooling charcoal to low temperatures. Under these conditions considerable amounts of almost any gas are adsorbed before a measurable pressure develops. Coconut charcoal being the most highly retentive is generally used for the purpose. The charcoal is first evacuated at elevated temperature to a pressure of the order of 10^{-2} mm. after which it is cooled by liquid air and put into communication, by means of a tap, with the apparatus to be evacuated. For the highest efficiency the pressure should first be reduced as far as possible with vacuum pumps and the charcoal bulb protected by a liquid air trap to condense vapours. The rate and degree of clean-up will depend on the quantity of charcoal used and on the accessibility of the latter. Unless wide-bore connections are used it is advantageous to employ more than one charcoal bulb. Greased taps exude vapour continuously and should be reduced to a minimum in vacuum apparatus. Under proper conditions it is possible to reduce the pressure to 10^{-5} mm. in a few hours (Kaye, "High Vacua," Longmans, London, 1927).

For the estimation of hydrocarbons in gases active charcoal is of great utility. It efficiently adsorbs vapour at the lowest partial pressures, the "breakpoint" (100% adsorption efficiency limit) is sharply defined, and the adsorbed vapour may be recovered in unchanged condition. In addition, there is great latitude in the rate at which gas may be passed. For the recovery of hydrocarbons from coal-, coke oven-, or other gas, in quantities suitable for analysis, a convenient apparatus is described by H. Hollings, S. Pexton and R. Chaplin (Trans. Inst. Chem. Eng. 1929, **7**, 102 ; *see also* Voss, J.S.C.I. 1930, **49**, 343T). Laboratory determinations of the vapour content of a carrier gas may be made with 15–20 c.c. of small-grain, active charcoal in a stoppered U-tube 2 cm. in diameter. This is first dried at 130°C. for about 30 minutes by passing 15–20 litres of air or nitrogen, and then cooled in a stream of the gas. A small volume of the gas for test is then passed and the zero weight of the tube taken against a counterpoise. The gas for test is then passed at rates up to 15 litres/hour and metered at the outlet on a wet test meter. Several different values of volume and weight-increase are obtained and plotted when an approximately straight line will result if the whole of the vapour present in the gas passed has been adsorbed. If this is found not to be the case the determination is repeated on smaller gas volumes and with a fresh sample of active charcoal. In the determination of vapour pressure a correction for the volume of the vapour removed should be made if this is significant.

Active charcoal is a most efficient medium for the thorough purification of gases from oil vapours, but is less efficient as a drying agent. For the purification and thorough drying of gases these should be subjected to the action of active charcoal followed by that of silica gel (*v.* ADSORPTION).

In assessing the value of active charcoal for any given purpose it is important to test it under the conditions in which it is required to be used ; for example, a charcoal required for benzole recovery would be tested with benzene at 7–8 mm. partial pressure while a charcoal for decolorising purposes would be tested by the adsorption of iodine or dye from solution.

INDUSTRIAL APPLICATIONS.—Active charcoal is widely used in industry for the recovery of valuable products which exist as attenuated vapours in unadsorbable gases, *e.g.* liquid hydrocarbons in natural gas, solvent vapours in air, benzole in coal and coke oven gases. The recovery processes are essentially the same in all cases and well illustrated by the recovery of benzole (*v.* COKE).

GASOLINE RECOVERY.—For the recovery of gasoline from natural gas and of uncondensed still vapours a compact and transportable plant is used (Edeleanu, J. Inst. Petroleum Tech. 1928, **14**, 296 ; Reisemann, Petroleum, 1932, **28**, 1). The principal parts are : the dust filter, two or more adsorbers each containing about 1 ton of active charcoal, the condenser, the separator, the steam economiser, and the blower. Prefiltered rich gas is passed through one or more adsorbers until gasoline begins to appear in the effluent gas, at this stage the charcoal will contain 12–16% by weight of hydrocarbons. The gas stream is then diverted to fresh adsorbers, and the saturated charcoal is heated to about 127°C. by means of steam coils embedded in the adsorbent. At the same time direct steam is blown through the charcoal to remove the gasoline which condenses along with the steam in the condenser and passes to the separator. At the conclusion of this operation air from the blower is passed through the charcoal to dry it, after which it is cooled and again opened up to the gas stream for a new cycle. The steam consumption is 3–4½ tons per ton of recovered gasoline. With natural gas the charcoal consumption is limited to mechanical loss which does not exceed 1 kg. per ton of recovered gasoline. Certain still vapours, however, cause a decline in activity of the charcoal which has ultimately to be replaced.

In the recovery of solvent vapours from air no depreciation of the adsorbent is encountered and it is claimed that it may be used many thousands of times before needing replacement through mechanical disruption.

Active charcoal is used on a large scale in Germany for the removal of hydrogen sulphide from town's gas. The hydrogen sulphide, by the action of oxygen in the presence of ammonia, is catalytically oxidised to sulphur, which is recovered from the charcoal by extraction with ammonium sulphide solution. The extract is worked up for sulphur (Engelhardt, Gas- u. Wasserfach, 1928, **71**, 290).

Active charcoal has also been used in Germany for dephenolising effluent gas-works liquor. The liquor is pre-filtered through towers packed with coke and iron turnings, after which it is warmed to 60°C. and filtered through beds of active charcoal. The adsorbed phenol is recovered from the charcoal by extraction with benzole from which the phenol is obtained by evaporation. Retained benzole is removed

from the charcoal by steaming, which conditions it for renewed contact with gas liquor. A high degree of purification of the liquor is attainable but the adsorbent depreciates through the accumulation of insoluble matter (F. Sierp, Gas- u. Wasserfach 1933, 76, 105).

In the purification of drinking water active charcoal has in recent years been used with success. Its use is confined to the final stages of purification for the removal of excess chlorine remaining after chlorination and of traces of phenol introduced through contamination of the water with factory effluents. These substances even in minute concentration give the water an objectionable taste The water, previously purified as far as possible by the usual means, is chlorinated and slowly filtered through beds of active charcoal. Highly polluted waters may be rendered potable by this treatment, the cost of which is estimated to be about $1 50 per million gallons of water (J. R. Baylis, J. Amer. Waterworks Assoc. 1929, 21, 787; F. Sierp, Gas- u Wasserfach, 1931, 74, 764).

Active charcoal has been used for some years in the sugar industry for decolorising, but there seems no likelihood at present that it will displace bone char which has so long been used for this purpose. Although active charcoal has a greater decolorising power it has a lower capacity for salts than bone char and its use appears to increase the quantity of molasses.

The use of active charcoal in respirators for protection against toxic gases is well known. Its high capacity for these substances, its versatility as an adsorbent, its instantaneous action and low resistance to breathing form a combination of properties so far not found in any other material. However, it affords but slight protection against certain substances, viz. hydrocyanic acid, arsine, cyanogen chloride, and none against carbon monoxide (Lamb, Wilson and Chaney, *l c.*).

Some further uses of active charcoal are: the purification of carbon dioxide in the fermentation industries, air conditioning; increase of storage capacity of cylinders for compressed acetylene; maintenance of a vacuum in the jackets of commercial containers for liquid air.

R. C.

CARBON BLACK *v.* CARBON, LAMPBLACK.

CARBON, COMPOUNDS OF.

Carbon tetrabromide, tetrabromomethane, CBr_4, is obtained by the action of bromine on carbon disulphide in the presence of iodine (Bolas and Groves, J.C.S. 1870, [ii], 8, 161; 1871, [ii], 9, 773). It is most conveniently prepared by the exhaustive bromination of acetone: 4 g. of acetone in 5 litres of water are mixed with a solution of 224 g. of sodium hydroxide dissolved in 750 c.c. of water, 84 6 g. of bromine are added in successive small quantities (0 5 c c.) and the mixture vigorously shaken after each addition. After 24 hours the supernatant liquid is siphoned off, the solid tetrabromide dried on porous earthenware and purified by sublimation (D.R.P. 70362; Friedl. 4, 11). It forms white, lustrous crystals of pungent odour, m p. 94°, b p. 101°/50 mm., 189 5°/760 mm. with slight decomposition, insoluble in water, soluble in alcohol, ether and chloroform. It exists in two enantiomorphs (Rothmund, Z. physikal. Chem 1897, 24, 705), both of which are bimolecular (Verstraete, Bull. Soc. chim. Belg. 1934, 43, 513; Solier, *ibid* 1931, 40, 403). The length of the molecule is 4 0 Å (Rumpf, Physikal. Z. 1930, 31, 791).

Carbon tetrabromide can be used for selective bromination of the side chain of alkyl benzenes (Hunter and Edgar, J. Amer. Chem. Soc. 1932, 54, 2025). Its action on sulphur and selenium, giving a mixture of products, has been investigated by Briscoe, Peel, and Rowlands (J.C.S 1929, 1766).

Carbon tribromide or hexabrooethane, C_2Br_6, is obtained by the action of bromine on ethylene dibromide or C_2HBr_5. It forms small rectangular prisms, soluble in carbon disulphide, insoluble in alcohol and ether, decomposing at 200° into carbon dibromide and bromine (Reboul, Annalen, 1862, 124, 271).

Carbon dibromide, tetrabromoethylene, C_2Br_4, white crystals, m p. 53°, is formed by the action of nascent hydrogen on the tribromide (Lowig, Annalen, 1832, 3, 292; Lennox, J.C S. 1862, 14, 209).

Carbon bromide, dibromoacetylidene, $C\,CBr_2$, is obtained from tetrabromoethane by removal of 2 mols. of hydrogen bromide. It is a liquid of b.p 76°, spontaneously inflammable in air and very explosive (Lemoult, Compt rend. 1903, 136, 1333, 137, 55). Lawrie (Amer. Chem J. 1906, 36, 487) showed it to contain a double bond *See*, however, Biltz, Ber 1913, 46, 142; *E. H Ingold, J.C.S. 1924, 125, 1528.*

Chlorotribromomethane, $CClBr_3$, m p. 55°, b.p. 160°, and **dichlorodibromomethane,** CCl_2Br_2, m.p 22°, b p. 135°, and **trichlorobromomethane,** CCl_3Br, m p. −21°, b p. 104°, are obtained by the action of bromine on chloroform at 250°–275° and are separated by fractional distillation (Besson, Compt. rend. 1892, 114, 223). The last compound is also obtained by the action of bromine on trichloracetic acid (*van't* Hoff, Ber. 1877, 10, 678).

Chlorotribromoethylene, $CClBr{:}CBr_2$, m.p. 34°, b.p. 203°–205°/734 mm., is prepared from chlorotetrabromoethane by removal of HBr (Denzel, Ber. 1879, 12, 2208).

$\alpha\alpha$ Dichloro $\beta\beta$-dibromoethylene,

$$CCl_2{:}CBr_2,$$

b.p. 172°/765 mm., f.p. below 0°, $d^{17.5}$ 2 3753, is obtained by the action of alcoholic potash on dichlorotribromoethane (Swarts, Bull. Acad. roy. Belg. 1898, [iii], 36, 519).

$\alpha\beta$-Dichloro-$\alpha\beta$ dibromoethylene,

$$CClBr{:}CClBr,$$

b p. 172°/765 mm., is a product of the action of aluminium bromide on carbon tetrachloride (Swarts, Bull. Acad. roy. Belg. 1898, [iii], 36, 519), as is also

Trichlorobromoethylene, $CCl_2{:}CClBr$, m.p. −12° to −13°, b.p. 145°–148° (Besson, Compt. rend. 1894, 119, 88).

Chloropentabromoethane, C_2ClBr_5, m p. 170° with vigorous decomposition, is obtained by the action of bromine on chlorotri- and chlorotetrabromoethane (Denzel, Ber. 1879, 12, 2207).

$\alpha\alpha$-Dichloro-$\alpha\beta\beta\beta$-tetrabromoethane,

$CCl_2Br{\cdot}CBr_3$,

is formed with dichlorotribromoethane by the action of bromine on α-dichlorodibromoethane. It evolves bromine vapour at 175° and melts with vigorous decomposition at 180° (Denzel, Ber. 1879, 12, 2207).

$\alpha\beta$-Dichloro-$\alpha\alpha\beta\beta$-tetrabromoethane,

$CClBr_2{\cdot}CClBr_2$,

melts at 191° (Swarts, Bull. Acad. roy. Belg. 1898, (3), 36, 519).

$\alpha\beta\beta$-Trichloro-$\alpha\alpha\beta$-tribromoethane,

$CClBr_2{\cdot}CCl_2Br$,

m.p. 178°–180°, is formed by the chlorination of C_2Cl_3Br (Besson, Compt. rend. 1894, 119, 88).

$\alpha\beta\beta\beta$-Tetrachloro-$\alpha\alpha$-dibromoethane,

$CClBr_2{\cdot}CCl_3$,

is obtained by the repeated chlorination of $C_2H_2Br_4$ (Bourgoin, Bull. Soc. chim. 1875, [ii], 23, 4) or bromination of C_2HCl_5 (Paternò, Gazzetta, 1871, 1, 593). It smells like camphor and can be sublimed.

$\alpha\alpha\beta\beta$-Tetrachloro-$\alpha\beta$-dibromoethane,

$CCl_2Br{\cdot}CCl_2Br$,

is formed by the action of bromine on tetrachloroethylene in sunlight (Malaguti, Ann. Chim. Phys. 1846, [iii], 16, 24).

Fluorotribromomethane, CBr_3F, a colourless, heavy, pleasant-smelling liquid, b.p. 107°, is obtained by heating carbon tetrabromide at 50°–60° with silver fluoride. Further treatment with silver fluoride yields—

Difluorodibromomethane, CBr_2F_2, a mobile liquid, b.p. 24·5°, f.p. below −80° (Rathsburg, Ber. 1918, 51, 669).

as-Heptachloropropane,

$CHCl_2{\cdot}CCl_2{\cdot}CCl_3$,

m.p. 32°, b.p. 247°–248°, is formed by the action of phosphorus pentachloride on pentachloroacetone (Fritsch, Annalen, 1897, 297, 312), by direct addition of chloroform to tetrachloroethylene under the influence of aluminium chloride (Böeseken and Prins, Proc. K. Akad. Wetensch. Amsterdam 1911, 13, 685; J.C.S. 1911, 100, 173) or by the action of chlorine on propylene chloride (Cahours, Annalen, 1850, 76, 283).

Hexachlorobenzene, C_6Cl_6, discovered in 1821 by Julin, is the final product of the chlorination of benzene and of many alkyl benzenes. It is also formed by direct synthesis when a current of 5·5 amps. passes at 42 volts for 1½ hours between carbon electrodes in a chlorine atmosphere. It forms colourless, silky needles, of m.p. 226° and b.p. 326°, is tasteless but has an odour resembling spermaceti. It is insoluble in water, acids, and alkalis soluble in alcohol, ether and hot oil of turpentine. It burns with a bluish flame, and decomposes into chlorine and charcoal on passing through a red-hot tube filled with glass or rock crystal. Strongly heated potassium burns in the vapour.

This compound was formerly regarded as carbon monochloride; its molecular formula was established by Bassett (J.C.S. 1867, [ii], 5, 443).

Carbon tetraiodide, tetraiodomethane, CI_4, is obtained by the action of aluminium iodide on a mixture of carbon tetrachloride and disulphide (Gustavson, Ber. 1881, 14, 1705). It forms dark red octahedra, of sp.gr. 4·32, the length of the smallest possible unit cube being 9·14Å (Hassel and Kringstad, Tekn. Ukeblad, 1931, 78, 230). It dissolves in various solvents and oxidises rapidly in solution (Dubrisay and Emschwiller, Bull. Soc. chim. 1935, [v], 2, 127).

Carbon subnitride, C_4N_2, is obtained by dehydrating the diamide of acetylene dicarboxylic acid:

$$H_2N{\cdot}OC{\cdot}C{:}C{\cdot}CO{\cdot}NH_2 = N{:}C{\cdot}C{:}C{\cdot}C{:}N + 2H_2O$$

(Moureu and Bongrand, Compt. rend. 1910, 150, 225). It forms fine white needles of m.p. 20·5°–21° and has b.p. 76°/773 mm., d_4^{25} 0·9703 and abnormally high molecular refraction and dispersion. The vapour resembles cyanogen in odour, irritating action, and the blue flame with which it burns, igniting spontaneously at 130°. Reactions with ammonia and amines are described by Moureu and Bongrand (*ibid.* 1914, 158, 1092).

Carbonyl chloride, Phosgene, $COCl_2$. Phosgene was first prepared by J. Davy by the action of sunlight on carbon monoxide and chlorine, and this direct combination method is still employed on the commercial scale, though it is now usually carried out in the dark with an activated carbon catalyst (Jacqué, Chim. et Ind. 1928, 19, 24). The most convenient laboratory preparation is by the action of carbon tetrachloride on sulphur trioxide:

$$CCl_4 + 2SO_3 = COCl_2 + S_2O_5Cl_2$$

(Giordani, Annali Chim. Appl. 1928, 18, 90), or on oleum or on sulphuric acid in the presence of infusorial earth (Grignard and Urbain, Chem. Zentr. 1919, III, 989). Phosgene is also formed by the action of carbon monoxide on certain chlorine compounds: nitrosyl chloride (Williams, U.S.P. 1746506), antimony pentachloride (Annalen, 1849, 70, 139), ruthenium, platinum or gold chloride (Manchot and Lehmann, Ber. 1930, 63, [B], 1221). For danger attending the use of carbon tetrachloride as a fire extinguisher owing to its conversion into phosgene in the presence of moisture, *see* carbon tetrachloride (p. 323; *cf.* Hamilton, Ind. Eng. Chem. 1933, 25, 539; Olsen, *ibid.* 541); the addition of ethylene dibromide is said to reduce this danger (Glaser and Frisch, Z. angew. Chem. 1928, 41, 263).

The mechanism of the photo-chemical production of phosgene has been investigated by many workers, whose explanations are based on the formation of active chlorine, $COCl$, or Cl_3. *See* Warming (Z. physikal. Chem. 1932, B, 18, 156), Schumacher and Wolff (*ibid.* 1934, B, 25, 161; 26, 453), Montgomery and Rollefson (J. Amer. Chem. Soc. 1933, 55, 4025; 1934, 56, 1089), Kassel (*ibid.* 1936, 56, 243).

Phosgene is a colourless gas, of b.p. 8°C., crit. temp. 182°C., and d_4^0 1·432. Its dipole moment is $1{\cdot}18 \times 10^{-18}$ (Smyth and McAlpine, J. Amer. Chem. Soc. 1934, 56, 1697) and its

ultra-violet absorption spectrum indicates a structure similar to that of formaldehyde (Henri and Howell, Proc. Roy. Soc. 1930, A, 128, 178). It has a penetrating, choking smell and is very poisonous, a concentration of 45 mg. per cubic metre of air being dangerous. Masks for protection against it contain, besides charcoal for adsorption of phosgene, a hydrolysing layer and an adsorbent for the hydrochloric acid thus formed (Nielsen, Z. ges. Schiess- u. Sprengstoffw. 1932, 27, 136, 208, 244, 280; Engelhard and Stiller, Z. Elektrochem. 1934, 40, 833). Hexamethylenetetramine is also recommended as an adsorbent (Jacqué, l.c.). An antidote to phosgene poisoning is urease, obtained from the soya bean (Svensson, Svensk farm. Tidskr. 1930, 34, 493, 509, 545, 565; 1931, A, 759). Phosgene dissolves readily in glacial acetic acid, benzene and other hydrocarbons, it dissociates on heating, and is very reactive. It is decomposed by water into carbon dioxide and hydrochloric acid, yields with alcohol chlorocarbonic ester, $ClCO\cdot OC_2H_5$, or carbonic ester, $CO(OC_2H_5)_2$; with ammonia, urea, and with aniline, diphenyl urea. Its reaction with ethylene has been investigated by Pace (Gazzetta, 1929, 59, 578), Varschavski and Doroganjevskaja (ibid. 1934, 64, 53) and Klebanski and Tschevitschalova (Compt. rend. Acad. Sci. U.R.S.S. 1935, 2, 42). Polymers of phosgene are described by Melnikov (Voennaya Khim. 1934, Nos. 2, 9; Chem. Zentr. 1935, I, 1650).

The detection and estimation of phosgene are usually required to be carried out in the presence of chlorine. The most satisfactory methods are the precipitation of diphenyl urea (Jacqué, l.c.) and the sodium iodide–acetone method of Olsen, Ferguson, Sabetta, and Scheflan (Ind. Eng. Chem. [Anal.], 1931, 3, 189).

Phosgene is used in the manufacture of di- and triphenyl methane dyestuffs.

Carbonyl cyanide, $CO(CN)_2$, is formed by direct union of carbon monoxide and cyanogen in ultra-violet light. It is a yellow, amorphous, non-volatile solid, dissolving in alkalis to a yellow solution and slowly hydrolysed by acid to carbon dioxide and hydrogen cyanide (Berthelot and Gaudechon, Compt. rend. 1913, 156, 1766).

Carbon monosulphide, $(CS)_x$.—When carbon disulphide is exposed to a silent discharge and then frozen on glass in liquid air, a subsequent slight rise in temperature brings about explosive decomposition into carbon monosulphide and sulphur (Klemenc, Z. Elektrochem. 1930, 36, 722). A polymeride is also obtained by exposing carbon disulphide to sunlight, or by ultra-violet irradiation of carbon disulphide and carbon tetrachloride (Doran and Gillam, J.S.C.I. 1928, 47, 259T), or by the action of thiocarbonyl chloride on nickel carbonyl:

$$xCSCl_2+xNi(CO)_4=xNiCl_2+4xCO+(CS)_x$$

Carbon monosulphide is a reddish-brown powder of sp.gr. 1·6, which can be compressed into a solid block of sp.gr. 1·83. It is a non-conductor of electricity, insoluble in water, alcohol, turpentine or benzene (Sidot, Compt. rend. 1869, 69, 1303; 1872, 74, 180; 1875, 81, 32) but giving a purplish-brown solution in conc. sulphuric acid, brown solutions in aqueous or alcoholic ammonia, ammonium sulphide, potassium hydroxide and potassium hydrosulphide and a red solution in nitric acid. It can be heated *in vacuo* up to 360°C. without change, but decomposes at a dull red heat into carbon disulphide and carbon.

Carbonyl sulphide, COS, discovered by Than in 1867, occurs in some mineral springs, and can be isolated from gases containing it by scrubbing with alkali and treating the resulting solution with acid. It is prepared by passing carbon monoxide over heated sulphur or with sulphur vapour through a red-hot tube, by the action of sulphuric acid on potassium or ammonium thiocyanate:

$$KCNS+2H_2SO_4+H_2O =COS+KHSO_4+(NH_4)HSO_4$$

(Hempel, Z. angew. Chem. 1901, 14, 865), by treating isocyanic esters with hydrogen sulphide:

$$2OC{:}N\cdot C_2H_5+H_2S=COS+CO(NH\cdot C_2H_5)_2$$

or by heating sulphur trioxide with carbon disulphide. Mustard oils treated with sulphuric acid yield carbonyl sulphide and primary amines.

Carbonyl sulphide is a colourless gas, of d (air=1) 2·1046, critical temperature 105°, and critical pressure 60 atm. It liquefies at 0° and 12·5 atm. to a colourless, mobile, highly refractive liquid of d_0 1·073, f.p. −138·2°, and b.p. −50·2°/760 mm., which dissolves sulphur and mixes with alcohol and ether but not water (Ilosvay, Bull. Soc. chim. 1882, [ii], 37, 294; Stock and Kuss, Ber. 1917, 50, 159). The gas has an unpleasant odour except when quite pure, and is a strong nerve poison. 0·8 c.c. of it dissolves in 1 c.c. of water at 13·5° and 756 mm. and is slowly decomposed into hydrogen sulphide and carbon dioxide; this reaction has been investigated by Thompson, Kearton, and Lamb (J.C.S. 1935, 1033). It is rapidly decomposed by alkalis yielding the alkali sulphide and carbonate. A white-hot platinum wire causes decomposition into sulphur and carbon monoxide, and the gas burns readily in air to carbon dioxide and sulphur dioxide and forms an explosive mixture with oxygen (Russell, J.C.S. 1900, 77, 356). Oxidation by bromine water or acid permanganate yields carbon dioxide and sulphuric acid; reduction to hydrogen sulphide by hydrogen and a catalyst is used for removing the gas from mixtures (B.P. 370978).

Carbonyl sulphide can be used for the synthesis of thio acids and of *s*-trisubstituted carbinols by means of organo-magnesium compounds (Weigert, Ber. 1903, 36, 1007).

The vapour density of carbonyl sulphide gives a molecular weight just below that required by the formula COS (Pearson, Robinson, and Trotter, J.C.S. 1932, 660), and the absorption spectrum from a hydrogen discharge tube indicates dissociation into carbon monoxide and sulphur (Lochte-Holtgreven, Bawn and Eastwood, Nature, 1932, 129, 869). From spectra and thermochemical data, the molecule has the linear structure $O{:}C{:}S$ (Zahn and Miles, Physical Rev. 1928, (ii), 32, 497; Bailey and

Cassie, Proc. Roy. Soc. 1932, A, **135**, 375; Boersch, Monatsh. 1935, **65**, 311); its infra-red and Raman spectra have also been investigated by Bailey and Cassie (Nature, 1931, **128**, 637), Bartunek and Barker (Physical Rev. 1935, (ii), **48**, 516), and Dadieu and Kohlrausch (Physikal. Z. 1932, **33**, 165).

Carbonyl azide, Carbazoimide, CON_6, obtained by the action of sodium nitrite on aqueous carbohydrazide hydrochloride, is a highly explosive substance, reacts with aromatic hydrocarbons to give pyridine bases and amines (Curtius and Bertho, Ber. 1926, **59**, [B], 565).

Carbonyl bromide, $COBr_2$, is obtained by the action of hot, conc. sulphuric acid on carbon tetrabromide (Schumacher and Lenher, Ber. 1928, **61**, [B], 1671). It is a colourless, fuming liquid, b.p. 64°–65°, d^{15} 2·52, of physiological action similar to phosgene but less readily hydrolysed by water. Above 150° it decomposes slowly into carbon monoxide and bromine (Lenher and Schumacher, Z. physikal. Chem. 1928, **135**, 85; Reerink, Rec. trav. chim. 1928, **47**, 989). The *oxime*, m.p. 70°–71° *in vacuo*, is obtained from bromine and oximino-acetic acid (De Paolini, Gazzetta, 1930, **60**, 700).

Carbonyl selenide, $COSe$, is obtained by passing carbon monoxide over heated selenium. It is a colourless, evil-smelling gas, of crit. temp. 121·1°±0·2°, condensing to a mobile liquid of d_4^{41} 1·812, and b.p. −22·9°±0·2°/725 mm., and a white solid of m.p. −122·1°±0·5°. The vapour density corresponds to the formula $COSe$ (Pearson and Robinson, J.C.S. 1932, 652).

Carbon sulphidoselenide, $CSSe$, is formed by treating ferrous selenide with carbon disulphide vapour at 650° and fractionating (Briscoe, Peel, and Robinson, J.C.S. 1929, 56). It is a yellow oil of b.p. 83·90°–83·95°/749·2 mm. Its physical and chemical properties have been investigated by the same authors (*ibid.* 410, 1048).

Carbon tetrafluoride, CF_4, is the most stable of the fluorides formed by the action of fluorine on charcoal (Ruff and Keim, Z. anorg. Chem. 1930, **192**, 249). It is also produced in the electrolytic manufacture of beryllium (Lebeau and Damiens, Compt. rend. 1926, **182**, 1340) and in the electrolysis of cryolite in a magnesia crucible (Treadwell and Köhl, Helv. Chim. Acta, 1926, **9**, 681). It is a gas which condenses to a liquid of b.p. −128° (Menzel and Mohry, Z. anorg. Chem. 1933, **210**, 257), f.p. −186·8°, and sp.gr. at the b.p. 1·3 (Klemm and Henkel, *ibid.* 1932, **207**, 73). 7·45 c.c. dissolve in 100 c.c. of water at 16° without hydrolysis. Carbon tetrafluoride is stable to heat and unreactive.

Dibromotetrafluoroethane, $C_2Br_2F_4$, is an oily liquid of b.p. 47·4° and f.p. −111·5°, formed by the action of bromine on tetrafluoroethylene in sunlight (Ruff and Bretschneider, Z. anorg. Chem. 1933, **210**, 176).

Hexafluoroethane, C_2F_6, b.p. −78·1°, m.p. −100·5°, is an unreactive gas formed with tetrafluoroethylene on burning carbon in carbon tetrafluoride (Ruff and Bretschneider, *l.c.*).

Tetrafluoroethylene, C_2F_4, b.p. −76·3°, m.p. −142·5°, is a gas resembling ethylene, produced on burning carbon in carbon tetrafluoride and isolated by conversion into the dibromo compound and treating the same with zinc and acetic acid (Ruff and Bretschneider, Z. anorg. Chem. 1933, **210**, 173).

Hexachloroethane, C_2Cl_6, m.p. 187°, is formed by passing an electric current between carbon electrodes in a chlorine atmosphere at a higher strength and voltage than for the production of hexachlorobenzene.

Iododifluoromethane, $CHIF_2$, b.p. 21·6°, and **Diiodofluoromethane,** CHI_2F, b.p. 100·3±0·5°, m.p. −34·5°±0·5°, are both stable in the absence of light and air (Ruff, Ber. 1936, **69**, [B], 299).

Carbon subsulphide, C_3S_2, is a red liquid which solidifies to a yellowish-red solid of m.p. −5°. It is best made by passing an electric discharge between carbon-antimony electrodes in carbon disulphide vapour (Stock and Praetorius, Ber. 1912, **45**, 3568). It is soluble in carbon disulphide, alcohol and benzene; the alcoholic solution decomposes on standing. It is stable to water, alkali, acid and chlorine water, and decomposes on heating *in vacuo* into carbon disulphide and a carbonaceous residue. It polymerises slowly at room temperature and rapidly at 100° to a coal-like, non-volatile substance, and combines with aniline to form thiomalonanilide, $CH_2(CS{\cdot}NH{\cdot}C_6H_5)_2$.

CARBON DIOXIDE.

Occurrence.—As carbon dioxide is the final product of the oxidation of carbon in organic compounds, it is of widespread occurrence. It issues from the ground in some places (volcanic districts) as a gas or dissolved in water, often under pressure (mineral water). In limestone districts the gas may be present to a considerable extent in caverns, wells, etc. Carbon dioxide is present in the products of respiration of man to the extent of about 4% in the exhaled air. It is formed by many processes of fermentation and by the atmospheric decay of animal and vegetable substances, the carbon dioxide evolved from decaying manure and from waterlogged soils being due to these processes.

Ordinary air contains between 0·03 and 0·04%, but this quantity may be increased considerably, particularly in busy streets, since the exhaust gases from petrol engines contain up to 13%.

It is also found in coal mines, where it is formed by the oxidation of the coal; after an explosion of "fire damp" it is known as "choke damp."

The percentage of carbon dioxide in various industrial gases is: blast-furnace gas about 11%, coal gas from retorts and ovens 2–4%, producer gas 4–5%, and water gas 5–7%.

It is also present in the gases from many metallurgical processes in which metallic oxide or carbonate is reduced by carbon.

As carbon dioxide is evolved by plant roots, the soil atmosphere contains rather more than atmospheric air.

Production.—Carbon dioxide can be obtained by passing air through a red hot coke bed. A minimum of excess air is used, giving a mixture containing a moderate amount of carbon monoxide in addition to the carbon dioxide. The hot gas mixture is then mixed with a little

excess air (secondary air) and passed into a combustion chamber containing a number of refractory brick baffles, where the carbon monoxide, hydrogen (from the action of water vapour in the primary air and coke, on the hot coke) and hydrogen sulphide (from sulphur in the coke), are oxidised to carbon dioxide, water, and sulphur dioxide respectively. The resultant gases, which may be cooled by being made to raise steam in a boiler, contain, with careful control of air addition, up to 18% carbon dioxide, mixed with the nitrogen and some oxygen from the air used, and an amount of sulphur dioxide depending on the sulphur content of the coke. They are then scrubbed with water in a tower containing limestone at a temperature of about 40°C. to remove dust and sulphur dioxide, and the carbon dioxide is removed by scrubbing with warm (30°–40°C.) potassium carbonate solution (15–20 g./100 g. solution). The solution from the scrubber then passes to a boiler, after having been preheated by liquor leaving the boiler, where it is heated to just over 100°C. by the gases leaving the coke bed or the secondary air combustion chamber, when the dissolved carbon dioxide is liberated. The liquor is cooled and recirculated round the scrubber. Sodium carbonate solution can be used in place of potassium carbonate, but its strength must be reduced on account of the lower solubility of sodium bicarbonate. It is necessary to carry out the combustion of the coke in two steps, since the gases obtained by passing air through red hot coke contain carbon monoxide which cannot be burnt completely by air in the presence of coke. Surplus heat from the hot gases is used for steam raising, the steam being used to drive the necessary machinery.

Carbon dioxide is concentrated from other gases such as water gas, when used for ammonia synthesis or hydrogen production. In this case, water gas containing about 5–7% carbon dioxide and about 40% carbon monoxide is passed over a catalyst with steam, which converts the carbon monoxide to carbon dioxide and hydrogen, and gives a gas containing about 30% carbon dioxide. This gas is then scrubbed with water under pressure (about 25 atms.) when the carbon dioxide is removed. The water emerging from the scrubber can be used to drive a water turbine and generate electric power or can be let down to atmospheric pressure directly. In either case the dissolved carbon dioxide is given off and the water recirculated. The carbon dioxide will contain hydrogen sulphide, and a little nitrogen, carbon monoxide and hydrogen. The hydrogen sulphide can be removed by passing the gas through iron oxide (bog ore) boxes.

Carbon dioxide is also separated in processes using the Linde Frank Caro process for separating and purifying gases by liquefaction.

When natural carbon dioxide is liberated from mineral water springs it often contains a little hydrogen sulphide, which can be removed by washing with potassium permanganate solution, and should the gas contain a large amount of air, it can be concentrated by washing with water under pressure.

Some carbonates readily evolve carbon dioxide on heating, and if the partial pressure of carbon dioxide is reduced during the heating, the gas is evolved at a lower temperature. Thus, natural forms of calcium carbonate, dolomite or magnesite when heated to redness in a current of steam, evolve carbon dioxide, which is collected after condensation of the steam.

Carbon dioxide is also produced by alcoholic fermentation during the manufacture of beer, etc. It is usually collected from enclosed vessels under a pressure just greater than atmospheric in order that air shall not be drawn into the carbon dioxide evolved. The gas from this source usually contains a little hydrogen sulphide, and various organic products and esters which give it an unpleasant smell. When required for mineral water manufacture and similar purposes, it is often purified by cooling and by-passage over active charcoal under pressure (Anon., Chem. and Ind. 1928, 47, 62). The charcoal is revivified by expelling the adsorbed impurities by steaming. The use of silica gel for this purpose in place of active charcoal is usually carried out under a pressure of about 80 lb. per sq. in., the gel being regenerated by heating. When these methods of purification are used, a number of purifying vessels are installed so that one is always available for regeneration. A chemical method of purification has also been used in which the carbon dioxide produced by a fermentation process is washed with dilute alcohol solution and then with water. The aldehydes and higher alcohols which are often present are removed by washing with potassium dichromate and sulphuric acid, the products of oxidation being removed by washing with glycerine (*see* Reich, Chem. Met. Eng. 1931, 38, 136, 271).

Carbon dioxide has also been prepared, when required for mineral water manufacture, by the action of acids (hydrochloric or sulphuric) on limestone or magnesite (giving magnesium sulphate solution, which is worked up), but carbon dioxide for this purpose is now often supplied in the liquid form, or in the solid form, known as *dry ice*.

When the ammonia soda process is used for the manufacture of sodium carbonate, the carbon dioxide is obtained from limestone kiln gases, which contain about 30% carbon dioxide. The kilns may be fired externally with producer gas and internally with coke to the extent of about 10% by weight of the limestone, air being blown through the kiln. When carbon dioxide for liquefaction is made by this method, the sulphur content of the coke is kept low because of the formation of sulphur dioxide. The gases are then washed with water and the carbon dioxide removed by washing with potassium or sodium carbonates (for 5 tons carbon dioxide per day the washing towers are 9 ft. diameter and 50 ft. high, and contain grids packed with coke and the liquor is circulated at the rate of about 1,200 gallons per minute), when the inert gases and unabsorbed carbon dioxide pass to atmosphere. The carbon dioxide is recovered by heating the solution. The use of triethanolamine, which is alkaline and forms carbonates with carbon dioxide, as an absorbent

of carbon dioxide has been proposed. The use of this absorbent has not yet been firmly established (*see* Reich, *l.c.*).

When required in small quantities, carbon dioxide is best prepared by the action of hydrochloric acid on marble or sulphuric acid on sodium carbonate.

Properties.—The specific gravity is 1·3833 (O_2=1) and *d* 1·9767 g. per litre at 0°C. and 760 mm. Hg.

The determination of the molecular heat of carbon dioxide at high temperatures is rendered difficult because of its dissociation into carbon monoxide and oxygen. From a review of the literature, Partington and Shilling ("The Specific Heat of Gases," p. 203, 1924) give for the true molecular heat at constant volume, in cals. per g.-mol., the following equation :

$$C_v = 6{\cdot}700 + 0{\cdot}0045t - 1{\cdot}02 \times 10^{-6}t^2$$

The values for $C_p - C_v$ given by the above authors are 2·051 at 0°C. and 2·039 at 20°C., and the ratio C_p/C_v is 1·303 at 20°C. (Partington and Cant, Phil. Mag. 1922, 43, 369).

Carbon dioxide is appreciably soluble in water, giving a solution which is acid to litmus. Its solubility in water is made use of industrially for separating it from other gases. The volume of carbon dioxide measured at 0°C. and 760 mm. Hg, dissolved by 1 vol. of water when the pressure of the gas less that of the water vapour is 760 mm. Hg, is given below (Seidell, "Solubility of Inorganic and Organic Compounds," 1919):

t°C.	0	10	20	30	40	50	60
vol. gas	1·71	1·19	0·88	0·67	0·53	0·44	0·36

The solubility of carbon dioxide in water at different pressures is given below ("International Critical Tables," Vol. III, p. 260, 1928):

t°C.	Pressure, atm.	c.c. gas.
20	25	16·3
	30	18·2
	40	22·0
	50	25·7
35	30	10
	40	14
	50	17
60	40	8
	50	10
	60	12
	70	14

Carbon dioxide is adsorbed by wood charcoal to a considerable extent (*see* Homfrey, Proc. Roy. Soc. 1910, A, 84, 99).

It diffuses through vulcanised rubber or balloon fabric about 2·5 times as fast as hydrogen, and a good deal faster than most other gases.

The vapour pressure of the liquid is :

t°C.	−56·6	−50	−30	−10
p atm.	5·1	6·7	14·1	26·1

t°C.	0	10	20	30
p atm.	34·4	44·4	56·5	71

The critical pressure is 73·0 atms. and critical temperature 31·1°C., and the density of the liquid is 0·460 g. per c.c.

The melting-point of the solid is −56·6°C. at 5·2 atms. and the density is 1·53 at −79°C., and 1·59 at −100°C. (*see* "International Critical Tables," Vol. III, p. 43, 1928).

The molecular heat of formation from graphite is 94·385 kg.-cals. ("International Critical Tables," Vol. V, p. 181, 1929).

Although carbon dioxide is not toxic, air containing more than 30% may prove fatal in 30 minutes on account of its suffocating action, but 4–6% can be inhaled for up to an hour without serious effects. The maximum safe limit in air is 2–3%. As the gas is practically odourless (it has a characteristic effect on the nose) and is dense compared with air, it is apt to collect in the bottom of vessels, pits, manholes, etc., no person, therefore, should descend suspicious pits, etc., unless provided with a gas mask and a life-line.

As carbon dioxide is the final product of the combustion of carbon it is a non-supporter of normal combustion; this property and its relative density to air are made use of in various types of fire extinguishing apparatus.

Carbon dioxide is essential for plant life, sugars being made from it under the action of sunlight in the presence of water.

The moist gas and its solution in water have acid reactions, and natural waters, which almost invariably contain some dissolved carbon dioxide, often, particularly in chalky districts, dissolve the limestone to give the bicarbonate, which is more soluble in water than the carbonate. Such water, on being heated, deposits the chalk because of the decomposition of the bicarbonate, or, if the carbon dioxide is present under pressure, allows the carbonate to be deposited when the pressure is reduced, causing the formation of stalactites or stalagmites. The deposition of carbonates on boiling the water is the cause of "fur" of kettles, "scale" in boilers, etc., the water being known as "temporary hard water."

Although carbon dioxide has been thought to cause corrosion of iron, it has been found that iron can rust under conditions which exclude the presence of any appreciable amounts of carbon dioxide. The corrosion of iron and steel by water depends to a large extent on the oxygen content and acidity of the water, and carbon dioxide may be present in sufficient quantity to affect the latter. Carbon dioxide gas seems to have little effect on the corrosion of iron (*see* U. R. Evans, "Corrosion of Metals," 1926).

For the equilibria between carbon dioxide, carbon monoxide, carbon, and oxygen, *see* Carbon Monoxide.

Carbon dioxide under the effect of suitable catalysts and conditions can be reduced to carbon monoxide and to methane.

The reaction

$$CO_2 + H_2 = CO + H_2O$$

is dealt with under Carbon Monoxide.

The reaction

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

has the following values for the equilibrium constant at constant pressure (partial pressures in atmospheres).

$$K_p = \frac{p^2_{H_2O} p_{CH_4}}{p_{CO_2} p^4_{H_2}}$$

T°K . .	681	709	765	773
Kp . .	3·13	2·64	1·69	1·58

(*see* "International Critical Tables," vii, 244, 1930).

When carbon dioxide mixed with excess *hydrogen is passed over an active nickel catalyst*, reduction according to the above reaction commences at 230°C. If the hydrogen content of the gas is insufficient, reduction to carbon monoxide occurs. Cobalt can be used in place of nickel but is less active and deposition of *carbon is more likely to occur* (*see* Sabatier and Senderens, Ann. Chim. Phys. 1905, [viii], 4, 424). Other metals may also be used and the choice of catalysts is stated to be wider if high pressures are used, but sulphur compounds are likely to poison the catalysts

Gaseous *carbon dioxide is used for the manufacture* of sodium carbonate by the ammonia soda process, ammonium carbonate and bicarbonate. Its use in sugar refining, mineral water carbonation, the making of pure alumina from bauxite and of salicylic acid from phenol has been *largely superseded by the use of gas made* from dry ice.

In some fire extinguishers the gas is generated by the action of acid on a carbonate with or without the addition of a foam stabiliser.

As carbon dioxide is essential for plant life and is the source of plant sugars, its use has been suggested as a plant fertiliser, but there are differing views on this use of carbon dioxide It has been found that the yields of tomatoes and cucumbers under glass have been increased by 20% and 16% respectively following treatment for 1–2 hours daily in an atmosphere containing 0·6% carbon dioxide for tomatoes and 0·9% for cucumbers The carbon dioxide necessary can be obtained from the flue gases of the boiler used for heating the glass house by absorbing the gas in an alkaline carbonate solution and liberating the pure gas by heating (*see* Owen, Small, and Williams, Ann Appl. Biol. 1926, 13, 560). The use of carbon dioxide for fertilising fields by increasing the amount of this gas in the atmosphere has been tried, but the results are doubtful Two methods have been used, the first by adding carbon dioxide gas to the atmosphere and the second by generating carbon dioxide on the ground by the use of special manures containing peat, charcoal and manganese peroxide. It is quite likely that the production of carbon dioxide by the fermentation and decay of farmyard manure is an important factor in its use.

While the application of carbon dioxide appears to have possibilities as a fertiliser, a good deal more work is necessary before conditions for its use can be laid down (*see* Miller, "Plant Physiology," 1931).

The ripening of apples in storage can be retarded by the use of carbon dioxide, and in an atmosphere containing up to 10% carbon dioxide *apples and some other fruit may be kept in* good condition long after their normal season.

Carbon dioxide is readily absorbed by alkalis, and caustic soda or caustic potash solutions are used to absorb the gas in quantitative determinations, the alkali usually being titrated *with acid using a suitable indicator. For the* determination of small amounts, such as occur in air, excess of barium hydroxide solution is used as the alkali; the carbonate is deposited and the solution back titrated with acid using phenolphthalein as the indicator.

Recording instruments for use on kiln gases, boiler flue gases, etc., are often used. Some of them make use of a difference in viscosity between air and the flue gas, small fans in each of the gases being rotated by an electric motor. Others use a katharometer in which the heat *loss from an electrically heated wire is measured*, and another depends on the variation in electrical conductivity of a solution of barium bicarbonate in equilibrium with a saturated solution of barium carbonate.

Liquid and Solid Carbon Dioxide.—*Carbon dioxide, when compressed and cooled*, forms a liquid which is sold in cylinders and is used for the manufacture of mineral waters, and in fire extinguishing apparatus, etc

For the purpose of making the liquid, the gas, purified as previously described, is compressed, *usually in three stages* (80 lb. *per sq. in*, 400 lb., and 900 lb), with a drying process using either solid calcium chloride, silica gel, etc, or by cooling between the first two stages. Drying is necessary, since carbon dioxide forms hydrates with water. At ordinary temperatures liquid carbon dioxide dissolves about 0·04% water, and at 10°C. this separates out as the hexahydrate, $CO_2,6H_2O$, which is liable to cause choking of pipe lines, etc. The gas leaving the final stage of the compressor is cooled, when the liquid carbon dioxide separates. Liquid ammonia is often used for cooling the carbon dioxide gas or liquid before its expansion.

When the liquid is expanded, solid carbon dioxide snow is formed and in recent years, a considerable amount of solid is made in this way and used mainly for refrigeration purposes. Although first produced over 100 years ago, the solid was first made commercially in 1924, since when the output has been enormous. The original method of manufacture was to let down liquid carbon dioxide to atmospheric pressure and to press the solid snow into blocks In this way, 1 ton of liquid gave 0·355 ton of solid with a power consumption corresponding to 208 k.w.h. per ton of solid. By making use of the phase diagrams and applying thermodynamic principles, however, the liquid is now let down in stages, and the power requirements have been reduced to 145 k.w.h. per ton of solid (Littler, J.S.C.I. 1933, 52, 533).

Since solid carbon dioxide, known as *dry ice* and under various other trade names, is used as a refrigerant and often is in direct contact with foodstuffs, its purity is of paramount importance, particularly as impurities tend to concentrate in the liquid and solid and very small quantities of some organic and sulphur compounds may give the dry ice an objection-

able smell. (Some impurities from industrial gases have to be reduced to less than 1 part per million.) Most of the methods used for purifying carbon dioxide gas have been given, but, in addition, the oil used for the lubrication of the compressors may cause serious contamination of the solid. A refined, odourless mineral oil or glycerine is used for lubrication, but care has to be taken that no overheating takes place, since this may cause the lubricants to decompose and result in an objectionable impurity.

For the Mollier curves for the solid-liquid-gas system, a knowledge of which is very important for the detailed understanding of the processes for the manufacture of solid carbon dioxide, *see* Maiuri (Ice and Refrigeration, 1936, **90**, 74).

In the Frick process for the manufacture of solid carbon dioxide, cooled liquid carbon dioxide at about 1,100 lb. per sq. in. is admitted, through a special expansion nozzle, into a cast steel cylinder closed with a movable lid at the top and by a hydraulically operated piston at the bottom. The admission of liquid is continued for a definite period (a few minutes) depending on the size of the cylinder, and when sufficient carbon dioxide has been expanded, the liquid supply is cut off and the bottom piston raised in order to compress the snow into, usually, a square block. The lid is then removed and the solid block ejected. The gas evolved during the process is used to cool the inlet liquid.

The Carba process does not make use of hydraulic pressure in order to make the solid blocks. In this process the converter has a filter cloth at the top and bottom and liquid carbon dioxide at about 1,100 lb. per sq. in. is expanded through a special nozzle into the converter. A mixture of solid and liquid carbon dioxide thereby collects on the bottom filter cloth, the surplus gas being compressed in two stages and returned to the system. When sufficient wet solid has been collected, a final charge of liquid is admitted to ensure the complete wetting of the solid. The inlet and exit lines are then closed and a bottom valve opened; this allows the pressure to drop suddenly and the liquid to solidify, forming one completely solid block which drops from the bottom of the chamber. The gas evolved from this stage is returned to the low-pressure part of the system. The uniformity of the solid produced by this process depends on a careful control of pressures and rates of flow. The filter cloth at the top of the converter is used to prevent solid from choking the exit gas lines.

The Maiuri process makes use of liquid ammonia for the cooling of the compressed carbon dioxide and is claimed to be more efficient than older processes in that the process is thermodynamically reversible whereas the others are not. In this process the carbon dioxide, compressed to a pressure of 85 lb. per sq. in., is cooled with water to remove the heat formed by compression. The gas is then cooled further by ammonia vapours from an ammonia evaporator and then passes into moulds cooled by the evaporation of liquid ammonia at a pressure of about 3 lb. per sq. in. absolute and a temperature of about −60°C. The temperature and pressure conditions are such that the carbon dioxide, under a pressure above the triple point pressure, is frozen solid, passing momentarily through the liquid state, giving a dense ice instead of carbon dioxide snow which would have to be compressed. Liquid carbon dioxide at a temperature of about −50°C. and at a pressure of about 100 lb. per sq. in. can also be made in a similar way. The evaporated ammonia is absorbed by weak ammonia liquor from which the liquid ammonia is subsequently produced by heating under pressure and condensation of the ammonia gas evolved. A description of the process is given by Maiuri in Ice and Refrigeration, 1936, **90**, 74.

The solid is usually sold in the form of rectangular blocks weighing about 50 lb. each or in the form of cylinders 7 in. diameter, 14 in. long, weighing 25 lb.

Dry ice passes directly into gas under an external pressure of 1 atm. of carbon dioxide, since the triple point is at a pressure greater than 1 atm. and, if the pressure of gaseous carbon dioxide is altered, the temperature of the solid varies. For this reason, the density of blocks of dry ice is usually made less than the maximum possible (actually about 1·4) so that the material is plastic to a small extent. Hence, when a block is moved about, the temperature drop which occurs on the outside of the block, although causing a certain amount of shrinkage, does not result in the block flying to pieces, since the material is plastic enough to allow the shrinkage stresses to be taken up.

Solid carbon dioxide passes directly into gas under ordinary conditions at a temperature of −78°C. giving a very clean and convenient source of low temperature for refrigeration purposes. Weight for weight, dry ice is about twice as effective for this purpose as water ice, and about three times on a volumetric basis. The solid is easy to handle in spite of its low temperature, because of its high latent heat and density, and because of the insulating properties of the blanket of heavy carbon dioxide gas surrounding it. In practice, with special containers making use of the insulating properties of the gas, the loss on storage is less than 1% per day and the length of storage is limited by the growth of solid carbon dioxide crystals which make the block mechanically weak. When transported in special railway containers, the loss is stated to be about 1½% per 24 hours.

The advantages of dry ice over water ice for refrigeration purposes are that the dry ice is much cleaner to deal with, it is a more efficient refrigeration agent because of its lower temperature, and it can be mixed in intimate contact with foodstuffs. Its use has the further advantage that owing to its effect on bacteria, foodstuffs, etc., do not decay as fast in an atmosphere of carbon dioxide as they do in air at the same temperature. Since it takes about fifteen times as much power to make dry ice as water ice, the cost of the former is considerably higher, weight for weight, than the latter.

Apart from refrigeration, solid carbon dioxide is replacing the liquid form where the gas is used for carbonating mineral waters, etc., since owing

to the absence of a heavy container necessary *for the liquid, the transport charges are very* much lower when the solid is used. When used for carbonating, the blocks of dry ice are placed *in a high pressure container and heated with* steam, when the gas is evolved under pressure (*see* Chem. Trade J. 1928, 82, 302; Littler, *l.c.*; Reich, *Chem. Met. Eng.* 1931, 38, 136, 271)

The use of dry ice as a means of obtaining "shrink fits" in engineering work has also been made.

Liquid carbon dioxide is used as a fire extinguisher, the solid being produced by its evaporation and directed through a special nozzle on to the fire. It is claimed that it is possible to walk through a moderate fire if this type of apparatus is used, by taking advantage of the local cooling effect produced by the evaporation of the solid.

It has also been proposed that liquid carbon dioxide should be used for blasting and mining operations, particularly in cases where there is a risk of fire if ordinary explosives are used. The principle used is to heat electrically or chemically a special cartridge containing liquid carbon dioxide and fitted with a disc which shears at a pressure of 10–15 tons per sq. in. The shearing pressure can be varied according to the requirements, and it is claimed that this method of blasting gives a true heaving action as distinct from a shattering action, resulting, in the case of coal mining, in the production of larger lumps and a smaller quantity of fine coal. The disadvantages are that a larger bore hole is required and that additional transport costs are involved (*see* Coll. Guard. 1927, 135, 286; 1928, 137, 238; Chem. Trade J. 1929, 85, 618; Iron and Coal Trades Review, 1930, 120, 724).

The liquid has also been used for driving torpedoes and for raising sunken ships.

S. W. S.

CARBON DISULPHIDE.

Thiocarbonic anhydride, sulphocarbonic acid, CS_2.

Introduction.

This compound was discovered by Lampadius *in 1796 by heating sulphur with charcoal.* Clement and Désormes in 1802 obtained the same product by treating red-hot charcoal *with elemental sulphur. Its chemical composition was established by Vauquelin.*

Developments in the methods employed for manufacturing carbon disulphide have followed very circumscribed routes, and even to day the only chemical reaction known to be in successful commercial operation is that by which it was discovered. Many attempts, which will be detailed later, have been made in the last few years to devise other technical methods of production, but none of them, so far as is known, has gone beyond the laboratory or the semi-plant stage. The actual technique of carrying out the direct synthesis has, however, advanced very considerably in the last few decades, largely due to the rise of the artificial silk industry, since carbon disulphide is one of the raw materials of the viscose process and the increased demand, and high purity of the product required by this new industry has called for increased attention *to the manufacture and rectification thereof.*

Until the beginning of the present century the only commercial method in use was that in *which reaction took place in retorts* made of refractory firebrick or cast iron which were heated externally by either coke, wood, or *producer gas, but in 1901 a revolutionary change* was introduced by the Taylor electric furnace process, in which the heat necessary for reaction was supplied from inside the furnace instead of from outside, as formerly. Manufacturing progress has advanced since 1900 along two main paths depending on relative costs of power and combustible fuels. In districts where cheap power is available there is no doubt that the electric furnace process has many attractions, but in general it can be stated that far more carbon disulphide is still made in externally heated retorts than by the electrothermal method.

The crude carbon disulphide formed in the retorts of either the electric or gas-heated process contains sulphur compounds as impurities, and careful purification is necessary before the product is fit for sale. Early purification methods usually depended on a combination of chemical and physical operations for the removal of these impurities, but recent developments have tended towards purely physical separation by distillation.

Manufacture in Externally Heated Retorts.

(a) Development of retort process.—C. Brunner in 1829 (Pogg. Ann. 1829, 17, 484) described the first apparatus to make carbon disulphide in quantity. This was constructed *of graphite and produced 12 to 14 oz. of product* in 2 hours. Brunner referred to the possibility of increasing the scale of his operation, and his *apparatus is interesting as it forms the basis of all* subsequent externally heated processes.

Schrotter in Germany (Ann. Chem. u. Pharm. *1841, 34, 297*) advanced *the manufacture by* using an earthenware retort 26·2 cm. diameter by 62·8 cm. high, glazed internally, which was *filled with charcoal and provided with a bottom* inlet for molten sulphur and a top exit for carbon disulphide vapour. This apparatus made 20 kg. of product in 12 hours.

Chandelon (Dingl. poly. J. 1848, 109, 352) used a grey pig-iron cylinder 20 cm. diameter by 70 cm. high and a zinc condenser which produced 6 litres of impure carbon disulphide in 6–7 hours from 2·5 kg. wood charcoal and 10–15 kg. sulphur.

Rapid progress was made in France between 1840 and 1860 by Peroncel, Deiss, and Gerard. Peroncel (Payen's Précis Chim. Industrielle, Paris, 2nd ed., 1851, 98; Dingl. Poly. J. 1851, 120, 91) constructed a cast-iron cylinder 2 m. high by 30 cm. diameter by 6 cm. wall thickness, and using either stoneware or zinc condensers produced 100 kg. of carbon disulphide per day. Every 5–8 days, however, the retorts became corroded through and had to be renewed.

Deiss (Dingl. Poly. J. 1856, 140, 133; 1861,

159, 436; Compt. rend. 1856, 42, 207) used earthenware or cast-iron retorts, 1 m. high by 40–50 cm. diameter mounted singly or four together in one furnace which was heated by furnace gases. Each retort was divided internally into two parts by means of a perforated shelf, the upper compartment being used as a charcoal container, and the lower serving as a sulphur vaporiser.

Charcoal was fed into the upper compartment at intervals of about 7 hours and after it had been heated for 1¾ hours in the retort, sulphur was fed at a known rate into the bottom portion of the casting and distilled upwards through the red hot charcoal to form carbon disulphide, which together with unconverted sulphur escaped to the condensers. The crude product contained 10–12% dissolved sulphur and was condensed in a long train of 18–20 cylindrical sheet zinc condensers which were luted into water to trap condensed liquid while the uncondensed vapours passed forward to the final plant exit after scrubbing through lime to remove sulphuretted hydrogen. Figures given by Deiss showing the increase in output and decrease in market price of carbon disulphide are interesting. In 1840 the price was 50–60 francs per kg., but by 1848 had fallen to 8 francs per kg. In 1856 the output had risen to 500 kg. per day from three furnaces and the selling price was 50 centimes per kg.

Gerard (Payen's Chim. Industr., 4th ed., 1859, 128) introduced retorts with an elliptical cross section in order to increase the available heating surface for a given volume of heated charcoal and by so doing made a very important improvement in the design of carbon disulphide retorts. Since charcoal is a very poor conductor of heat and it is essential to ensure that the whole contents of the retort are at a uniform temperature, any method whereby this can be achieved without increasing the flue temperature outside the casting must inevitably result in a considerably increased retort life. Gerard's cast-iron retorts were 6½ ft. high, 4 ft. 8 in. by 1 ft. 6 in. in cross section, with a wall thickness of 1¾ in.; and produced about 570 lb. of product per day at a claimed efficiency of 90% on sulphur and 40% on raw wood charcoal employed.

When using unrefined sulphur the retorts needed cleaning every fortnight, but on purified sulphur they could be kept working for two months.

Galy-Cazalat and Huillard (B.P. 2085, 1857; Dingl. poly. J. 1858, 149, 31) constructed an earthenware apparatus of a new type in which the heat necessary for reaction was provided by burning part of the charcoal charge in the lower part of the furnace to which molten sulphur was fed at the top. This process would be both expensive in fuel and dangerous to operate owing to risks of explosion.

A plant erected at Swozowice, near Cracow, by the Austrian Ministry of Agriculture to provide supplies of carbon disulphide for use in the wine industry for destroying *Phylloxera* (vine-louse) was described by Navratil (Dingl. poly. J. 1878, 227, 289), Winkler (*ibid.* 1878, 228, 366), and Mrowec (*ibid.* 1879, 232, 86). Sulphur was extracted by means of carbon disulphide from a local earth containing 14–15% sulphur and was then converted into carbon disulphide by the ordinary process in earthenware retorts 2·25 m. high and elliptical in cross section (1·33 m. by 0·95 m.). The crude product containing 8–10% of dissolved sulphur was purified by distillation.

The earthenware retorts were very unsatisfactory and could not be prevented from leaking, and, in addition, they needed to be cleaned out every fortnight owing to accumulation of impurities. This plant did not work long, and was replaced by a more modern installation at Zalatna in Hungary, described by Farbacky (Z. angew. Chem. 1893, 7, 225) which operated with cast-iron retorts 2·52 m. high, elliptical cross section (1 m. by 0·56 m.), and lined internally with a 2·5 cm. layer of refractory paste to protect the metal. These were mounted in firebrick settings heated by gas, and had an average life of 8 months with a maximum variation of 2½–15 months. Two earthenware retorts in this plant lasted only 4 days each.

Manufacturing practice in this country in 1870–90 was described by Singer (J.S.C.I. 1889, 8, 83). Cast-iron or earthenware retorts were used about 6 ft. 6 in. high, elliptical cross-section 20 in. by 12 in., and had a wall thickness of about 2 in. Each retort was surrounded by a 4-in. mantle of firebrick, with a space of from ½ to ¾ in. between it and the retort to protect the metal from flame impingement, the settings being coal or coke-heated. Sulphur was melted in a cast-iron box heated by flue gas from the setting and the liquid sulphur was run by gravity into the bottom of the retort through a side arm which protruded through the furnace wall and was closed by a door. This side arm also served for removing charcoal ash from the retort once a week. A lid with two branches or hoppers was fitted to the top of the retort casting, and while one of these was used to vent the retort to atmosphere while cleaning or charging with charcoal, the second provided the opening through which fresh charcoal could be fed to the retort. A further branch pipe led away from the charcoal feeding hopper at an angle and conducted the carbon disulphide vapours to the condensing system through a capacity vessel which served to trap excess sulphur coming forward from the retort. Condensation of the vapours took place in a 30-ft. Liebig's condenser luted into water, under which the heavy carbon disulphide was collected and run to storage tanks while the uncondensable vapours were passed up a tower fitted with shallow trays over which vegetable oil was circulated to absorb residual carbon disulphide vapour. The oil was distilled to recover the carbon disulphide and was then returned to the system. Sulphuretted hydrogen was absorbed in a similar tower fed with milk of lime and the sweetened exit gas then passed to atmosphere.

Each retort made from 4 to 5 cwt. of carbon disulphide per day, but it is not clear whether the crude condensate from the Liebig's condenser was re-distilled to remove sulphur which would inevitably be present. Singer's paper is interesting as it provides an early reference to

the practice of pre-roasting charcoal before charging to the retorts. Holt and Millard (B.P. 14912, 1895) claimed an increase in yield of carbon disulphide from the ordinary cylindrical retorts by using an additional take off pipe at the bottom of the retort, thereby allowing, at will, the reaction gases to pass more than once over the heated charcoal before passing to the condenser. This process could not be successful owing to the continued reversal of direction of flow.

Scheuer (Z. angew. Chem. 1900, 14, 152) summarised a number of statistics on carbon disulphide manufacture, and also described its uses in detail. A plant constructed by Eckelt

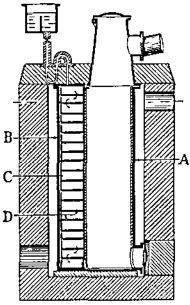


Fig. 1.

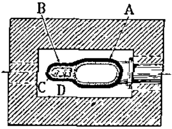


Fig. 2.

was described by Schuberg (Z chem. Apparatenkunde, 1905, 1, 10), in which Schamotte (refractory clay) retorts were used. The importance of this paper lies in the fact that it is the first reference to vaporisation and preheating of sulphur in a preheater external to the main retort, and marks a big step forward in the manufacturing technique.

Courtaulds, Ltd., and A E. Delph (B.P. 180175, 1921; G.P. 364524; B.P. 549351; U.S.P. 1754708) attempt to decrease the corrosive attack of sulphur vapour on iron at the high temperature of reaction by coating the inside of the retort with a thin layer of aluminium produced by the following procedure. This retort is one third to one-half filled with a mixture of 93 parts by weight of granulated aluminium, 5 parts of aluminium oxide, and 2 parts of ammonium chloride, and then rotated under vacuum about a horizontal axis for 3 hours at 800°C. in order to fix the aluminium firmly to the iron surface. If the coating then produced is insufficiently thick, the process is continued at 850°C. for a further 3 hours It is very difficult to ensure a completely uniform aluminised layer on cast iron and if corrosion starts at a fault in the aluminium, the iron sulphide formed underneath the surface layer rapidly causes blistering of the whole protective surface and destroys its usefulness

Considerable attention was paid to the manufacture of carbon disulphide in Germany after the war and rapid progress towards really efficient plants was made, especially by the I G. Farbenindustrie and by Zahn & Co, of Berlin

The fundamental advance made by the I G. workers was in the direction of increased throughput per retort, and a series of patents was taken out on the superheating of sulphur prior to entering the main reaction chamber.

The master patent covering the general principle of superheating sulphur is G P. 521337 (B P. 237716, F.P. 583319; Swiss P 117161), by E. Legeler, and claims the separate evaporation and superheating of sulphur prior to its entering the retort which is heated to reaction temperature.

Patents of addition to the above described apparatus for carrying out the operation. In the first of these (G.P. 521336, 1926; B P. 282049; F.P. 34609, 1928, U S.P. 1793181) the sulphur superheater consists of a pipe arranged inside the retort setting alongside the main retort, of length calculated to give the requisite heating to the molten sulphur which is fed into it from a melting vessel situated above and outside the setting The second addition patent (G.P. 478378, 1927, B P. 291382; F.P. 36081, 1928) deals with a sulphur preheater which is cast as an integral part of the main retort but separated from it by a retaining wall, the only communication between the superheating chamber and the main retort being by means of an opening at the bottom. This design of retort is illustrated by Figs 1 and 2, taken from the patent specifications, which show a vertical section through the retort and a plan respectively.

A indicates the main retort and B the superheater made as one piece in either cast iron or cast steel, but with a separating wall as shown Both retort and superheater are lined with refractory brick in order to protect the casting from the action of the sulphur vapour, and the superheater is either packed with earthenware Raschig rings or fitted with baffles C in order to increase the heat transference to the molten sulphur and to increase its time of passage through the superheater. The sulphur then flows in a zigzag path through the superheater, passing from baffle to baffle by means of staggered slots indicated by D.

A further addition patent (G.P. 472189; B P. 300579) describes separately heated super-

heating retorts of roughly the same shape and one-third to one-half the size of the main retort. The superheaters are arranged in the retort bench so that one of them can deliver to one or two main retorts. Suitable internal filling materials such as broken firebrick, earthenware rings, etc., may be used to increase the available heating surface of the superheater.

Koref in 1910 (p. 341) had shown that the reaction between carbon and sulphur vapour, both initially at about 850°C., is exothermic. The large negative heat of reaction found when the starting materials are at room temperature is almost entirely due to the large negative heats of dissociation of the sulphur molecules S_8 and S_6 in passing from the vapour phase at 440° to that at 850°C., where dissociation to S_2 is almost complete. In all early plants for manufacturing carbon disulphide, the sulphur was fed to the retorts as liquid at about 140°C. and had to be preheated to reaction temperature in the lower part of the charcoal bed under very inefficient conditions of heat transfer. This inevitably reduced the carbon disulphide producing capacity of the unit, since a large proportion of the mass of hot charcoal was below reaction temperature. By designing apparatus in which sulphur could be vaporised and superheated to 850°C. or thereabouts before coming into contact with charcoal a very considerable increase in output per retort was immediately achieved at the expense of operating and maintaining the vaporising equipment, which, if properly designed, could be made relatively small compared with the size of the retorts themselves.

The well-known chemical plant manufacturing firm of Zahn & Co., G.m.b.H. (Berlin) have several apparatus patents, the chief of which are summarised below:

G.P. 433588 (1925) which proposed to increase the heating surface and also the life of elliptical retorts by widening out the bottom portion and by casting ribs into this widened base in order to obtain more rapid vaporisation of the sulphur. The ribs are found to be unsatisfactory in practice owing to the tendency for slag to accumulate between them with consequent increase in difficulty of cleaning and decrease in heat transfer through the slag layer.

G.P. 467929, 1925 (B.P. 261990, 1926; F.P. 672766, 1929), describes a complete continuous process in which the sulphur is freed from impurities by melting in a box provided at its lower end with two compartments, one working and one spare, which serve as separators for both heavy and light impurities. Molten sulphur thus purified overflows from the middle of the separator into the base of a retort of elliptical cross-section of the type described in the previous paragraph, broadened at the base with ribs cast in the broadened portion in order to increase the heating surface. Carbon disulphide thus formed is led to a continuous distillation plant which is described in detail in the section on purification.

G.P. 489934 (1927) claims the production of carbon disulphide in small, elongated, vertical, cast-iron retorts which are tiled internally.

A description of a modern Zahn plant with photographs is given by Schofield (Chem. Age, 1932, **27**, 504).

In America, Griswold and the Dow Chemical Co., Midland, Michigan, U.S.A., have four patents (U.S.P. 1705619; 1719509, 1929; 1785080, 1930; 1848346, 1932) dealing with methods and apparatus for preheating sulphur prior to feeding to vertical retorts of the externally heated type. Various designs of preheater are described, *e.g.* preheaters cast in the base of the retort as an integral part of the casting, preheaters built separately into the furnace setting and connecting to the base of the retorts, etc. For details, see the patent specifications.

The use of earthenware retorts persists to the present day in certain countries, *e.g.* Spain and the Balkans, and several articles have appeared recently describing the operation of such installations in Spain. Bohle (Chem.-Ztg. 1924, **48**, 785; *ibid.* 1931, **55**, 198) and Caddick (Chem. Age, 1928, **19**, 536) give details first of the use of carbon disulphide for extracting olive oil from the husks of olives after pressing (p. 343), and secondly of its manufacture. The retorts are of earthenware made on the site, and are 2 m. high by 0·5 m. diameter by 15 cm. wall thickness, arranged four in a furnace and heated by coal. Pine charcoal in pieces 4 in. diameter is fed in at the top, and solid sulphur is charged from the top through a 3 in. diameter refractory tube leading to the underside of a grid fixed 8–10 in. from the retort bottom where it vaporises and rises through the charcoal placed on the grid.

Bohle (*l.c.*) gives data as to production and yields from these earthenware retort plants as follows:

With 20 retorts, sulphur being fed to the battery at the rate of 600 g. every 4 minutes for 6 hours, followed by a pause of 2 hours during which no sulphur is fed, and so on; thus feeding sulphur at the rate of 3,240 kg. in 24 hours, 3,000 kg. per day of crude carbon disulphide is produced. The yields are not so bad as are generally expected from the older types of plant, the usage of sulphur per ton of pure carbon disulphide being 1·17 tons, compared with an average of 0·95 ton sulphur per ton with a modern tiled cast-iron retort installation. Retorts are stated to last often from 2–3 years and cost only about 600 pesetas (£37) each.

(*b*) Discussion of retort process. (1) *Retorts.*—It has been shown how the retort process developed relatively slowly from the early stages of manufacture until quite recently, the original retorts made of earthenware being replaced first by cast-iron retorts and latterly by castings lined internally with fireclay tiles; while in some places the original method is still in use.

The main problem confronting the manufacture of carbon disulphide is the intensely corrosive nature of sulphur vapour, especially above 600°–700°C. Since the only metal known to be inert to sulphur, viz., aluminium, is unsuitable for these temperatures, and since all metals containing iron are readily attacked, the problem is serious.

Cast iron has been used almost exclusively for

retort manufacture on account of its cheapness, since mild steel is not capable of withstanding the temperatures employed (900°–950°C. without softening), but the former must be protected by an internal lining of firebrick tiles which immediately reduces the heat transfer through the retort walls. Also in order to obtain the requisite degree of strength in a retort 10–12 ft. high by 2–3 ft. diameter, the wall thickness must be at least 2–3 in., which necessitates very heavy castings. A further objection to cast iron is its "growth" at high temperatures, which may be as much as 6–8 in. in a 12 ft. casting, and causes serious difficulties if rigid connections are required between the retorts and the condensing equipment.

Attempts have been made to work with cast steel, or special alloy steels of much greater tensile strength than cast iron, which can therefore be made in thinner metal, but the decreased weight and only slightly increased life of such retorts are more than offset by the considerably greater initial cost of the alloy steels per unit weight.

The fundamental objections to the primitive earthenware retorts are, first, the difficulty of making them completely gas-tight, and secondly, the limitation in size caused by the material itself, which adds considerably to the operating costs when small units have to be employed.

Further, the relatively enormous wall thickness (6 in. for 18 in. diameter retorts in Spain) necessary for stability increases the heat wastage considerably owing to the poor conductivity of earthenware.

An elliptical cross section is of importance in providing both a stronger retort and an increased surface area through which heat can be transmitted from the furnace to the interior of the charcoal bed, and the best modern practice uses cast-iron retorts about 12 ft. long, elliptical in cross-section with axes about 4 ft. by 1 ft. 6 in., and wall thickness 3 in., lined internally with $\frac{3}{4}$ in. thick tongued and grooved firebrick tiles which are set in special cement. The castings are provided with a side opening near the bottom for removal of impurities and addition of sulphur, either as liquid from a luted feed box situated in the front wall of the furnace or as vapour from a boiler and superheater adjacent to the retort setting. A top casting bolted to the main retort is provided with side outlet for the carbon disulphide vapour and a top hopper into which preheated charcoal is fed to the retort at intervals. The retorts are mounted singly, or two or three together in a suitably designed furnace setting, and are fired externally by burning producer gas or other suitable fuel with air in a combustion chamber so designed that the whole area of the walls is uniformly heated. Great care must be taken to ensure that no direct flame impinges on the castings, as the life of the latter is considerably decreased by local overheating.

The average life of a good tile-lined retort which has been used carefully, and in which the tiles have been carefully set, is about 8–10 months, although certain cases are known in which a life of 18–20 months has been attained. It is inadvisable to allow a retort to cool down to ordinary temperatures after a period of use if it is to be restarted, as by this procedure the tiles tend to become loosened, and attack of the iron sets in more rapidly after production is recommenced.

The feed of sulphur to each retort must be interrupted for some hours at roughly three-weekly intervals for cleaning purposes. This operation consists of opening the door on the side opening at the bottom of the casting, raking out all the charcoal and ash left in the unit, and then slicing down the walls with chisel-ended pokers to remove wood ash which has partially fused to the tile lining. If not removed this ash causes arching of the charcoal and severely decreases both the heat transference through the retort walls and the available retort space in which reaction can take place. The operation is a very unpleasant one, as small quantities of sulphur inside the retort immediately ignite when the retort is opened and the slicing is normally carried out in an atmosphere seriously contaminated by suffocating sulphur dioxide fumes.

(ii) *Sulphur.*—Purity of the sulphur to be used for carbon disulphide manufacture is of fundamental importance owing to the accumulation of siliceous and carbonaceous residue from impure sulphur which settles out either in the retort bottom if liquid sulphur is fed direct to the retorts, or in the vaporising equipment if sulphur vapour feed is employed.

In the majority of early retort processes the sulphur was fed as solid into a cast-iron vessel set into the brickwork surrounding the main retort, and melted therein by radiation through the furnace wall. The molten sulphur then flowed continuously by gravity into the bottom of the retort through a lute and was distilled upwards through the charcoal in the retort, where it reacted to form carbon disulphide, which, together with sulphuretted hydrogen and other impurities, was led away to the condensing plant from an exit pipe at the top of the casting. In this process all impurities in the molten sulphur passed into the base of the retort and settled there, forming a heat insulating layer on the bottom. In addition, a sticky mass of liquid sulphur and fine particles of charcoal collected in the lower part of the reaction zone owing to the poor heat transference retarding vaporisation of the sulphur, and this complicated very considerably the regular routine operation of emptying and cleaning.

The advantages over the old liquid sulphur feed which are obtained by feeding sulphur vapour to the retorts are manifold. First, a considerably increased output per unit is obtained, since the amount of heat required inside the retort for preheating sulphur to reaction temperature is greatly decreased, this effect being intimately connected with a considerable economy in fuel and in the capital cost of an installation for a given daily output. G.P. 521337 of the I.G. describes this fact and claims that by regulating the quantity of sulphur fed, and the degree of superheating, the necessary temperature can be maintained by the heat of reaction.

In addition, any residue from the sulphur is

collected in the vaporising equipment from which it can be cleaned out and disposed of conveniently without opening up the retort; and finally the fine charcoal ash in the base of the retorts is kept friable so that the retort cleaning operation is simplified.

The cost of sulphur is the largest single item in the cost sheet for finished carbon disulphide and all possible methods of decreasing losses must be rigidly examined and adopted. One of these most serious losses occurs as sulphuretted hydrogen, which is formed by reaction between sulphur and residual hydrogen contained in the charcoal fed to the retorts. The formation of excess sulphuretted hydrogen affects the efficiency in two ways: first because of the sulphur it contains, and, secondly, inasmuch as it finally leaves the plant saturated with carbon disulphide vapour which is difficult to recover as such, and which, by reason of its high vapour pressure and density, represents a high weight loss of product.

(iii) *Charcoal.*—A good grade of lump beech or birchwood charcoal is used for carbon disulphide manufacture and a rigorous specification is necessary to ensure a uniformly high quality of material. Certain features must not be overlooked in purchasing charcoal, amongst which the following are considered to be the most important:

(*a*) The ash content must be as low as possible, and not higher than 2% by weight. In order to ensure this, no bark must be present, and all pieces of charcoal must be clean and free from dirt. This significance of the ash content of charcoal is easily seen when reference is made to the retort cleaning operation previously described.

(*b*) The particle size must be uniform, preferably between 1 in. and 4 in. cube, without dust; in order to prevent excessive packing or arching in the retorts and a uniformly even internal structure of the charcoal is essential.

(*c*) The charcoal must have been retorted under carefully controlled temperature conditions, in practice between 400° and 500°C. If made from wood at higher temperatures, cracking of residual hydrocarbon oils takes place inside the charcoal structure and a very unreactive product is formed, while at lower temperatures carbonisation is incomplete.

Wood charcoal as purchased contains from 80–88% carbon, 1–2% ash, 4–5% moisture, 3–4% hydrogen as hydrocarbons, and 5–10% oxygen which is present as an adsorbed carbon-oxygen complex of the type $CxOy$. Before this material can be used efficiently in the manufacture of carbon disulphide it must be pre-heated to about 750°–800°C. in order to remove all water, and as much as possible of the residual hydrogen and oxygen initially present in the raw charcoal. In the pre-roasting a considerable loss in weight occurs, and a good reactive batch of charcoal will lose up to 25% of its weight at 800°C., under which conditions the roasted product will contain from 96–97% carbon, 1–2% ash, 0·5–1·0% hydrogen, and 1–2% oxygen. This material is fed direct from the roasters into sealed containers which can be discharged into the carbon disulphide retorts out of contact with air.

G.P. 453504, 1924 (B.P. 236577; F.P. 600136; Swiss P. 116810; U.S.P. 1615659) of the I.G. Farbenindustrie covers the pre-heating of wood charcoal to 1,000°–1,200°C. in special pre-heating furnaces before use, but it should be noted that although a high pre-heating temperature has the desired result of eliminating hydrogen and oxygen more completely from the charcoal, the reactivity of the latter is considerably reduced as the temperature is raised. A more useful patent of the I.G. (B.P. 283267, 1924) relates to a method of activating wood charcoal by the action of sulphur vapour at high temperatures; any carbon disulphide formed in this activating process being collected and distilled. Other methods of activating charcoal have been proposed, among which may be cited U.S.P. 1992832 (1935) by Mootz in which the material is impregnated with a small quantity of caustic soda.

Several attempts have been made to eliminate the trouble caused by incipient fusion of charcoal ash on the walls of the retort. G.P. 492318 (B.P. 333090; F.P. 682843; U.S.P. 1795132) of the I.G. refers to the addition of inert infusible material such as silica, bauxite, etc., to the charcoal in quantities up to 15% by weight, which acts as a collector for the ash and carries it away to the base of the retort where it can be removed by suitable means. A serious disadvantage of this method of dealing with the problem would be the increased quantities of material to be handled.

A recent patent of the Chem. Fabr. Kalk G.m.b.H. (G.P. 605576) proposes to carry on the reaction with sulphur and charcoal mixed with inert materials such as bauxite or magnesia, and to supply the heat required by burning part of the charcoal charge. The use of an expensive raw material like charcoal fuel, apart from the danger involved, could not be justified on economic grounds.

The monograph by Kausch "Der Schwefelkohlenstoff," published by Julius Springer, Berlin (1929), contains very comprehensive information on all aspects of carbon disulphide manufacture. In it are quoted production figures (p. 128) for a retort plant as supplied by Zahn & Co., Berlin:

CS_2 output per retort per day	=700–750 kg.
Sulphur used per tonne CS_2	=950 kg. (90% yield).
Dried wood charcoal per tonne CS_2	=210–220 kg.
Coal for heating retorts per tonne CS_2	=450–500 kg.
Steam per tonne CS_2	=530 kg.
Power per tonne CS_2	=13·3 k.w.h.

(1 tonne=1,000 kg.)

It seems likely that the figures for retort output would be very considerably increased if sulphur vapour were fed to the retorts.

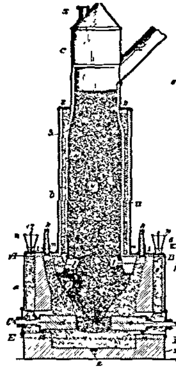
Manufacture in Internally Heated Retorts.

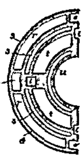
(*a*) *Development of the Electric Furnace Process.*—The original electric furnace for the production of carbon disulphide was designed by

E. R. Taylor about 35 years ago and operated by the Taylor Chemical Co., at Penn Yan, N.Y., America.

Full details can be obtained from the various

Fig. 5.





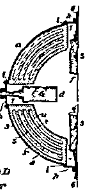
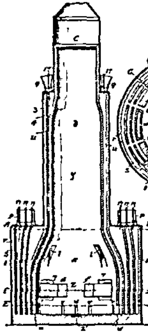


Fig. 3. Fig. 6.



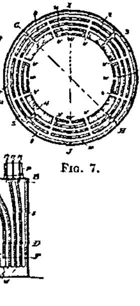


Fig. 7.

Fig. 4.

patent specifications (B P. 25182, 1901; 16556, 1902; G.P. 150826; 150980; 162629; F.P. 324409; 384356; U.S.P. 688364, 1901; 702117; 805501; 871971, 1907) and from articles which have appeared from time to time in the literature; *cf.* Taylor, Trans. Amer. Electrochem. Soc. 1902, 1, 115; 1902, 2, 185; Z. Elektrochem. 1903, 9, 679, 982, J. Franklin Inst. 1908, 165, 141; and also Ind. Eng. Chem. 1912, 4, 557, in which development of large size furnaces from small-scale plant erected at Pittsburg in 1893 is outlined.

The essential features of the Taylor furnace are shown in Figs. 3, 4, 5, 6 and 7, which are taken from the patent specifications.

Fig. 3 shows a section in elevation through the electrodes, and Fig. 4 shows a cross section in elevation at right angles, the figures being taken from the patent specifications. In Fig. 3 is shown the position of the electrodes *d*, D, near the bottom of the furnace shaft, which is represented as filled with charcoal; in Fig. 4 they are seen at *d*. At *k* (Fig. 3) are pipes through which are passed broken carbons, *i.e.* refuse from the factories of carbons for arc lights, for the purpose of reinforcing the main carbons, these pass down, upon, and over the ends of the main carbons, and convey the current *from the electrodes to the charcoal.* The intermediate conductive material protects the electrodes proper from the intense heat and eroding action and thereby prolongs their life. It also tends to steady the current, fluctuations *being mainly due to variations in power and not* to changes of resistance in the furnace itself The charcoal for the reaction is fed into the furnace through the opening (Fig. 3). Preferably four electrodes are used in this construction, supplied with two-phase alternating current. Provision is made for keeping the metallic portions of them comparatively cool by feeding cold sulphur on to them through the inlets shown as *o* (Fig. 3), and which can be replenished through the hoppers *n*, the sulphur passing into the annular chambers shown below the hoppers, seen in detail in Figs. 5, 6, and 7. The interior of the furnace is thus filled with sulphur, which is gradually melted and finds its way to the reaction zone. By this construction, the heat that would otherwise be radiated from the external walls of the furnace is absorbed, and no outside lagging is needed. The furnace is 16 ft. in diameter and 41 ft. high It needs much less care and is easier to manage than one of the small iron or clay retorts generally used.

In working, charcoal is put into the charger above the bell and the opening sealed. The charcoal falls into the shaft of the furnace as often as there is room for it, the charger being replenished from time to time. The shaft should be kept filled with charcoal and the internal spaces filled with sulphur; thus there is no loss of heat by radiation and the heat absorbed in melting the sulphur is returned to the furnace

Electricity is supplied in such quantity that the electrodes are not submerged in the melted sulphur to such an extent as to restrict the passage of the current. Usually, *the electricity* passes from the one electrode to the other immediately opposite, but the direction can be changed at any time so as to pass to the adjacent electrode, thus burning out any piers or

"scaffolds" that may form in the corners which would prevent the regular descent of the charcoal charge. The sulphur within the working chamber *z* soon becomes melted, and its level rises more or less nearly to the top of the electrodes. As it approaches the hot zone, the sulphur is vaporised and rises through the charcoal which, when sufficiently heated, combines with it, forming carbon disulphide vapour which ascends through the charcoal in the shaft, and passes out through the pipe *x* to a condenser. Aluminium bars, 6 in. wide and $\frac{5}{8}$ in. thick, connect the insulated electrodes with two Stanley inductive type dynamos, each of 330 kilowatts capacity, run, as a rule, by water-power. The average voltage is about 50.

Regulation of the furnace output is achieved by altering the sulphur feed which controls the level in the electrode space to which molten sulphur rises, and thus alters the resistance of the furnace.

Taylor states that the furnaces run for 8–12 months at an average output of 14,000 lb. carbon disulphide per day before cleaning is necessary, the average outside shell temperature under these conditions being 60°–70°C. indicating the degree to which heat is retained by the sulphur channels in the walls.

Haber (Z. Electrochem. 1903, 9, 399) gives figures for sulphur and charcoal consumptions as 1·00 and 0·24 tons per ton of carbon disulphide respectively, while Kausch (*op. cit.*) states that the power consumption lies between 1,000 and 1,200 k.w.h. per ton. It is therefore obvious that the Taylor furnace has no application to districts where cheap power is not available, while a further disadvantage of such a large unit is that considerable variations in output necessitated by fluctuations in trade are not readily obtained. Also it is stated that when closing down for cleaning purposes, one month at least must be allowed for each furnace to cool down.

An electric furnace of a type different from the Taylor design was patented by the Chem. Fabrik Griesheim-Elektron (B.P. 174040, 1921; G.P. 383416, 1921; F.P. 542518; U.S.P. 1549812; Can.P. 277731), in which the Taylor arc was replaced by resistance heating in a vertical shaft furnace between a fixed bottom electrode and a movable top electrode.

The invention lies in the fact that wood charcoal itself after pre-heating has a sufficiently high electric conductivity to allow a column of charcoal several metres high to be heated throughout to a uniformly high temperature at which rapid reaction with sulphur vapour occurs, thus permitting considerably greater outputs of carbon disulphide than in the older types of furnace in which a large portion of the charcoal charge acted as a cooler for the reaction products.

The shaft furnace is shown in Fig. 8, which carries at the bottom a fixed electrode B, above which the shaft is constricted in order to increase the temperature in the region of the sulphur feed D, which is connected to a heated vessel E. The furnace shaft is filled with pre-heated wood charcoal and the top movable electrode F rests freely in this charcoal column, being surrounded by charcoal fed in from the hopper G. H is the exit for the reaction products and leads to a condensing plant.

Movement of the top electrode F is obtained by means of the rope K and pulley system J_1, J_2, J_3.

A patent of addition to the above (B.P. 260969, 1926; G.P. 439694, 1925) relates to a device for collection and removal of the slag formed by reaction between the charcoal ash and sulphur residues. The bottom electrode is hollowed out into the form of a crucible in which the molten slag collects and is run off from time to time. The reservoir of slag serves, first, to protect the electrode from attack by

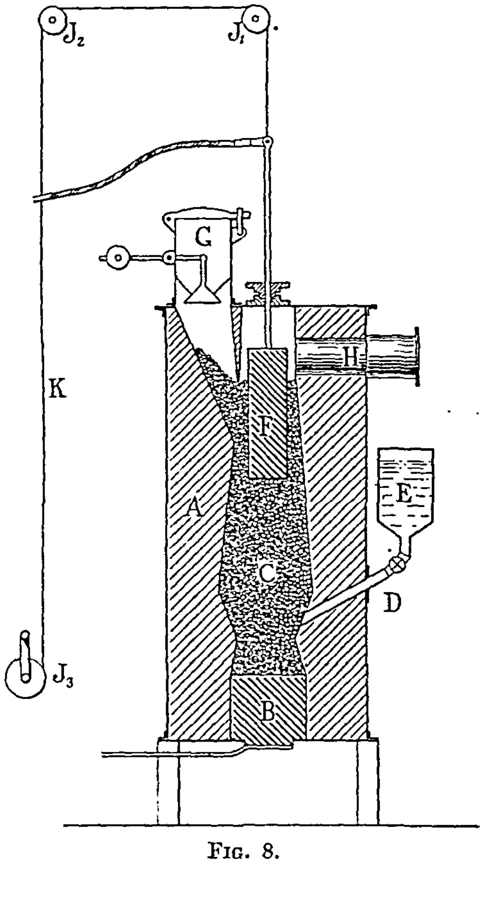


FIG. 8.

sulphur, and, secondly, to make better contact between the electrode and the charcoal charge which dips well below the surface of the molten slag.

The advantages of the vertical shaft furnace are discussed at length in Kausch (*op. cit.*), in which the following points are made:

(1) Small size of furnace, *e.g.* for 2·5 tonnes CS_2 per day, only 2·5 m. diameter, due to larger heated zone.

(2) More permanent character of brickwork than mild steel retorts. Furnaces can be shut down and restarted without difficulty due to cracking, etc.

(3) Cleaner working of electric furnace.

(4) Consumptions—power, 1,400 k.w.h. per

tonne CS_2; sulphur, 0 96 tonne per tonne CS_2; charcoal, 0 22–0·25 tonne per tonne CS_2.

Richter (Trans Amer. Electrochem. Soc. 1922, 42, 253) described an electric furnace operated by the Brown Co, Berlin, New Hampshire, U.S A. (U.S P. 1312800), which consists of a vertical cast iron cylindrical shell lined with refractory brick, and contains water cooled electrodes near the bottom which are fed with 2-phase 440 v. alternating current. A resistance bed of broken arc carbon is spread between the electrodes, and the wood charcoal rests upon this The same paper presents an analysis of the thermal balance of the carbon disulphide reaction and shows that the thermal efficiency (i e the amount of heat needed for the reaction compared with that which is actually put into

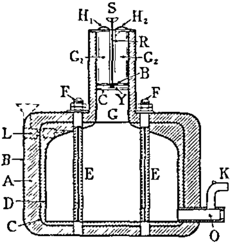


FIG. 9.

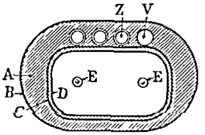


FIG. 10.

the furnace) is only 31%, most of the remainder being lost by radiation. A valuable set of tables of thermal data on sulphur and carbon disulphide is also given.

A considerable number of patents have been taken out on the electric furnace process which cannot be described at length A list of the patent numbers, with remarks on the more important, is given below, and further information may be obtained either from the original specifications or from Kausch (*op. cit*, pp. 92–103).

A. Walter (G.P. 413777, 1923) described a vertical shaft furnace which contained charcoal heated by a luminous arc in the base, and a sulphur-feed vessel heated electrically. Charcoal pre heaters were arranged in the top of the shaft. Complicated electrical apparatus is described for automatic regulation of the furnace.

H. Schulz (Berlin) obtained three patents (G.P. 407656, 1923; 438037, 450170, 1925) for a process and modifications thereto which consist essentially of a fireclay-lined rectangular metal retort with rounded corners, 2 m. by 3 m. cross-section and 2½ m. high, capable of producing 500–700 kg. carbon disulphide per day. The retort is heated by two vertical carbon resistances which ensure uniform heating of the charcoal charge, while sulphur vapour, which is pre-heated to reaction temperature by radiation from the retort, is introduced at the top, the exit for carbon disulphide being at the bottom.

Charcoal pre-heaters are arranged in the furnace lining and can be withdrawn bodily and placed in a special charging hopper in the top of the retort which prevents contact of the preheated charcoal with air.

Diagrams of this apparatus are given in Figs. 9 and 10, which are taken from Specification No 450170.

The outside metal case of the retort B is lined with refractory brick A as insulation, and this in turn has a further metal wall C which is protected from attack by the lining D, which is gas-tight and forms the wall of the reaction space

E, E are two resistance heaters connected to two electrodes F, F, which are spaced so that the distance between them is sufficient to produce the required reaction temperature. The resistors are suitably protected from the reaction gases

In one side wall of the furnace is built a device L for melting and vaporising sulphur which passes into the retorts, and after conversion the carbon disulphide is removed to the condensing plant *via* K.

G represents the filling arrangement for charcoal, which is preheated in metal containers Z, fitting into cylindrical recesses V cut in the front wall of the furnace (Fig. 10). The charcoal containers are closed by two overlapping flaps, which can be opened from above by a rod and are placed in the hoppers G_1 or G_2. When the lids H_1 and H_2 have been closed, thus sealing the interior of the furnace, the flaps in the containers are dropped and the hot degassed charcoal drops into the retort G_1 and G_2 are used alternatively as required

Schulz claims a purer product with this plant than is obtained by the ordinary retort process, owing to the fact that the charcoal is at uniformly high temperature throughout.

A detailed description of Schulz's plant is given by H. Rabe (Chem.-Ztg. 1926, 50, 609–611), in which the power consumption is stated to be 700–800 k.w h. per 1,000 kg. of product

G P. 433425 (W Buchner) and F.P. 340846 (Soc. Anon. L'Ind. Verrière et Dérivs.) (J S C.I. 1904, 23, 828) described a modified form of electric shaft furnace which has four pairs of electrodes fixed at intervals up the shaft.

The Studien-Gesellschaft für Wirtschaft u. Ind. (Munich) (G.P. 440863, 1925, and Swiss P. 125705) use either silicates or calcium carbide as resistance material, and place the wood charcoal on grates made of these materials. Little significance attaches to this proposal.

Zahn & Co. (G.P. 543874, 1930) propose the manufacture of carbon disulphide in electrically heated retorts in which the heating is from outside, the retort metal being protected as usual by refractory brickwork.

C. E. Taylor (U.S.P. 1596902, 1926) describes a modification to the original Taylor furnace in which a vertical shaft furnace having a bottom fixed electrode of cast iron and an upper movable carbon electrode is used. The furnace is more efficiently lagged than the original design, although the annulus of sulphur in the furnace wall which is melted by radiation from inside is still continued, with an additional sulphur feed through an annulus in the device carrying the upper electrode. The space between the electrodes is filled with broken graphite and pre-heated wood charcoal is fed on top of this. Apart from detail, the principle underlying this furnace seems to be the same as that of the I.G. shaft furnace described previously.

A modification of the Brown Co. furnace (*v. supra*) is patented in U.S.P. 1737566 (1929), where the earlier design is altered by lagging the whole furnace shaft with an annular space containing electric resistance material which can be separately heated in order to keep the inside shaft at a uniform temperature. In addition, the previous method of adding molten sulphur at the top of the shaft is substituted by a sulphur vapour feed between the two electrodes in the base of the shaft.

Two patents of the Dow Chemical Co., Michigan (U.S.P. 1892191; 1902668, 1933) describe an electric furnace which is characterised by a plurality of electrodes with separate switches, and several sulphur vapour inlets controlled by valves.

(*b*) *Discussion of the Electric Furnace Process.*—The great advantage of the electric furnace processes, whether of the arc or resistance type, over the gas-heated retorts lies in the fact that the source of heat for the former is inside the walls of the furnace.

It has been shown that a refractory earthenware lining is essential in all carbon disulphide apparatus for protection of the metal work, and while in the electric furnace this conveniently fulfils the dual function of protector from corrosion and heat insulator, in the retort plant where the heat is brought in from outside, the lining is a serious drawback because of its low heat conductivity.

Further, the thickness of the brick lining in the electric furnace can be increased to any desired figure, since this becomes a heat insulating layer and decreases the amount of heat lost through the furnace walls by radiation.

Since the electric process consumes approximately 1,000 k.w.h. per ton of carbon disulphide, a cheap source of power is obviously necessary for economic working, but given this, there seems little doubt that the electric furnace has the advantage, if only because of the decrease in danger due to the absence of flame in the retort building.

The Taylor furnace has the drawback of all large single units, *viz.*, the difficulty of conveniently meeting fluctuations in demand for the product, but this difficulty is largely overcome by the later designs which have been described.

With regard to pre-heating of charcoal and sulphur prior to reaction, the same remarks apply to the electrothermic as to the retort process, and whether the pre-heating is done by means of gas or electricity, it is absolutely essential to degas the charcoal in order to remove hydrogen, etc., and extremely desirable to work with a sulphur vapour feed entering the reaction zone at the normal reaction temperature.

Other Methods of Preparation of Carbon Disulphide.

In view of the difficulties connected with the manufacture of carbon disulphide from carbon and sulphur many alternative processes have been proposed which are described in detail in Kausch (*op. cit.*, pp. 103–114). A short summary of the most interesting of these is given below, but so far as is known no commercial application has been found for any of them.

(*a*) *Manufacture from Hydrogen Sulphide and Carbon.*—A. Walter (B.P. 306220, 1916; U.S.P. 1193210) proposed to prepare carbon disulphide by passing hydrogen sulphide over strongly heated carbon,

$$2H_2S+C=CS_2+2H_2,$$

and a similar method has been patented by H. Oehme and Chem. Fabr. Kalk G.m.b.H. (B.P. 314060, 1929; G.P. 484569; F.P. 675709), in which 70% conversion of the hydrogen sulphide to carbon disulphide at 900°C. is claimed. In addition to the above patent, B.P. 334856 (G.P. 488103) claims the recirculation to the conversion system of the unconverted hydrogen sulphide after carbon disulphide has been condensed, and a second addition patent (B.P. 358249; G.P. 517337) works with a mixture of hydrogen sulphide and carbon dioxide, which is converted to carbon disulphide, carbon monoxide, and hydrogen. After removal of the disulphide, a valuable fuel gas is obtained.

The reaction equilibria in the system H_2S, CO_2, H_2O, CS_2 have been studied by Terres and Wesemann (Angew. Chem. 1932, **45**, 795).

(*b*) *Manufacture from Sulphur and Hydrocarbons.*—The reaction between sulphur and sulphur compounds and hydrocarbons has also been investigated, *e.g.* methane and gases found in natural gas require a very high temperature (1,000°C.) for reaction, and this at once gives rise to the difficulty of getting sufficient heat into the reaction system to produce appreciable quantities of product. Unsaturated hydrocarbons, *e.g.* acetylene, react at lower temperatures (400°–500°C.), but the cost of acetylene makes such a proposal uneconomic. The following patents deal with this aspect of the subject: Reaction between methane, or hydrocarbon gases containing methane, and sulphur, or hydrogen sulphide at 1,000°C. with or without a carbon catalyst, I.G. Farbenindustrie (G.P. 476598, 1927; B.P. 293172; F.P. 648889; U.S.P. 1735409) and I.C.I. Ltd. (E.P. 331734, 357994; U.S.P. 1907274).

Reaction between unsaturated hydrocarbons (e.g. acetylene) and sulphur or sulphides at 400°–500°C. (Komlos, Komlos, and Engelke, B P 265994, G P. 469839, Swiss P 126816)

(c) *Manufacture from Sulphur Dioxide and Carbon*.—Rassow and Hoffmann (J. pr. Chem. 1922, [ii], **104**, 207) investigated the reduction of sulphur dioxide by carbon, and showed that the reactions were very complicated, and that the yield of carbon disulphide was too low to be of commercial importance

The production of carbon disulphide by this method has, however, been patented by L P. Bassett (B P. 20716, 1913), and by the Dow Chem Co (U S P. 1350858).

(d) *Miscellaneous*.—Carbon oxysulphide, **COS**, is readily formed by reaction of carbon monoxide and sulphur at temperatures below 600°C. with a yield approaching 100%, *cf.* Lewis and Lacy (J. Amer. Chem Soc 1915, **37**, 1982), Stock and Seelig (Ber. 1919, **52**, [B], 681), and Cross (J. Chim phys 1935, **3**, 825); and is decomposed catalytically into carbon disulphide and dioxide The equilibrium constant of the latter reaction at working temperatures of 500°–600°C is about 0 3, which indicates that unless one or other of the reaction products can be removed from the system continuously, the yield of carbon disulphide can never exceed 30%, *cf* Stock (Ber 1924, **57**, [B], 719) and Cross (*l c*) In spite of the technical difficulties involved in a process of this type, two patents have been taken out covering the above reactions by the Badische Anilin u Soda-Fabrik (G P 398332, 1922, and G P 413718, 1924)

The benzole fraction of the oils obtained from coal tar and coke oven gas manufacture contain small quantities of carbon disulphide, and quite recently a method of recovering this material by means of the xanthate reaction (p 343) has been brought forward—Hoffert and Hancock, B P 416404 (1934)—which consists in using a methyl alcohol solution of caustic soda to form sodium methyl xanthate which separates from the benzole, and recovering the carbon disulphide from the xanthate by acidification and subsequent distillation

Collection and Purification of Crude Carbon Disulphide

The reaction product passing away from the retorts consists of a mixture of inert gases, carbon disulphide, sulphur vapour, sulphur spray, hydrogen sulphide, carbon oxysulphide and smaller quantities of other volatile sulphur compounds These gases are usually passed into a water-sealed main in which the bulk of the carbon disulphide is collected and run to stock tanks as crude material containing up to 3% of dissolved sulphur, and quantities of hydrogen sulphide, etc. The uncondensed gas contains a high percentage of hydrogen sulphide and varying quantities of carbon disulphide vapour, depending on the temperature at which condensation in the hydraulic main has taken place, this gas must be treated for the recovery of carbon disulphide, after which it may be sent to waste or the sulphur recovered by the usual methods

It will be convenient to deal with the rectification in sections, (a) the purification of the bulk of the carbon disulphide formed by condensation and (b) the recovery of carbon disulphide from the exit gases.

(a) Purification of Crude Carbon Disulphide.

Early methods of purification consisted generally of a combination of physical and chemical processes, in which, for example, the crude carbon disulphide was distilled from the sulphur residue and then treated with caustic soda or milk of lime to remove hydrogen sulphide. Deiss (Dingl. poly. J 1861, **159**, 436; *ibid* 1863, **170**, 295) used large batch stills capable of holding 5 tons of crude material which took 3–4 days to distil. Heating was by means of closed steam pipes in the boiler, but the last traces of disulphide were removed from the residue of sulphur by means of live steam Sulphuretted hydrogen was removed from the distillate by agitation with caustic soda Bonière (Dingl poly J. 1864, **171**, 443) and Millom (Wagner's Jahresber Chem. 1868, 928) distilled the crude material from stills in the boilers of which the carbon disulphide was mixed with either caustic soda or milk of lime

Cloez (Compt rend 1869, **69**, 1356) first distilled the crude product and carried out a final purification by agitation with mercury to remove traces of hydrogen sulphide

Singer (J S C I 1889, **8**, 83) first removed sulphuretted hydrogen by counter current washing with milk of lime and then distilled the carbon disulphide.

Later methods which also relied on chemical purification are those of Obach. (J pr Chem 1882, [ii], **26**, 281), Friedburg (Ber. 1875, **8**, 1617), Palmieri (Z anal. Chem. 1882, **21**, 254), and Ruff and Golla (Z anorg Chem. 1924, **138**, 31)

References to methods of removing odour from carbon disulphide are given in Chem.-Ztg 1925, **49**, 121, 329, 350.

Little interest was shown in improved technical methods of purification until quite recently, the practice being to eliminate impurities one by one by a series of distillations, first to remove hydrogen sulphide and volatile impurities, then to remove sulphur and high boiling impurities, followed by a final distillation to eliminate last traces of both types of impurity. Since, however, the demand for a very pure product to supply the artificial silk industry has increased rapidly, considerable attention has been paid to this aspect of the problem chiefly by continental manufacturers.

The I G. Farbenindustrie has a series of three patents relating to methods of continuous distillation (G.P. 436998, 1924; B.P. 238489; F.P. 596526; U.S P. 1672948; G.P. 438072, 1925; B.P. 254676, F.P. 606841; U S P. 1728686; G.P. 439766, 1925; B.P. 260236; F.P. 622452; U.S P. 1699255, 1733171).

The first two of these patents refer to distillation in two columns, connected in series by an overflow pipe between the boilers, the first of which serves to remove volatile impurities at the head, while in the second sulphur and

non-volatile matter collect in the boiler, and pure carbon disulphide distils continuously at the head and is condensed.

The *third*, represented diagrammatically by *Fig.* 11, *modifies the earlier two-column distillation* apparatus in an ingenious manner. A and B represent the two packed distillation columns mounted in suitable heat insulating material provided with reflux condensers A^1, B^1, and boilers A^2, B^2, respectively.

Crude carbon disulphide is fed continuously to the top of column A, from which hydrogen sulphide and other volatile impurities pass away through the reflux condenser A^1, and a secondary condenser D, to the recovery plant. Carbon disulphide condensed here returns to column A as reflux, and flows down the column until it reaches a point where the temperature is approximately the boiling-point of carbon disulphide, when it distils as vapour contaminated with traces of sulphur and hydrogen sulphide through the pipe X to the top of column B. Sulphur contained in the feed to A flows downwards into the boiler A^2, in which a temperature of 120°C. is maintained, and this sulphur can then be recovered continuously or intermittently from A^2 in a pure liquid state.

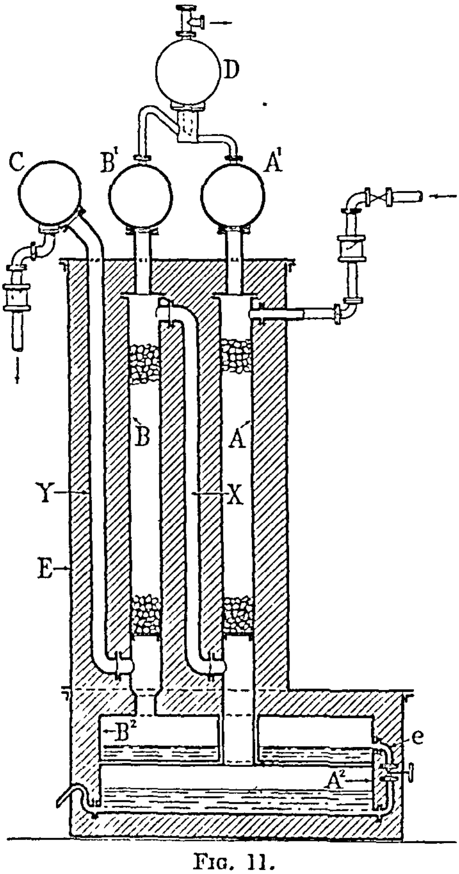


FIG. 11.

The vapours entering B from X are condensed in B^1 and D, which is common to both columns, and flow down B as liquid feed until at a point near the bottom of the column the boiling-point of pure carbon disulphide is reached, when pure vapour distils up the pipe Y to the condenser C, in which pure carbon disulphide free from sulphur and hydrogen sulphide condenses and runs to stock. The liquid collecting in the boiler B^2, which is maintained a few degrees above the boiling-point of pure carbon disulphide, consists of a weak solution of sulphur in carbon disulphide, and this is fed *via* the pipe *e* into A^2 for removal of its carbon disulphide content as desired.

Zahn & Co. (G.P. 467929; B.P. 261990; F.P. 672766 and 37206, 1926), in their patent for a complete carbon disulphide process, the first section of which has already been described, lead crude carbon disulphide *via* a siphon 12 into a steam-jacketed distillation vessel 13 (Fig. 12), in which sulphur contained in the crude material slowly accumulates, and is removed from time to time by pipes 15 to the heated separator 14, in which the carbon disulphide contained in it is vaporised *via* 17 into the main vapour pipe from the boiler, and the sulphur is removed from the bottom and led back to the retorts. *(For the details of the design of the separator the specification must be consulted.)* Vapour passes from the boiler to the partial

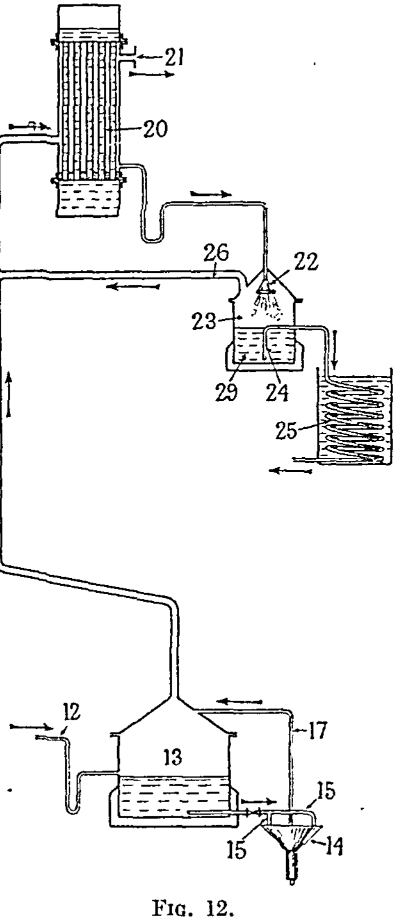


FIG. 12.

cooler 20 in which the carbon disulphide is condensed and separated from the bulk of the hydrogen sulphide, which passes *via* pipe 21 to a Claus kiln for recovery of sulphur. The condensate from 20 still contains traces of dissolved hydrogen sulphide which are removed by spraying into a heated separator 23 which contains boiling, or nearly boiling, carbon disulphide. On entering this vessel the remaining hydrogen sulphide is driven off from the carbon disulphide, and led back *via* 26 into the main vapour pipe, while the now purified product is siphoned *via* a pipe into the final condenser 25, from which it flows to stock.

The chief features of this process are, first, that the temperature of the partial condenser 20 is maintained fairly high in order to decrease the solubility of hydrogen sulphide in the condensed carbon disulphide, although this fact immediately increases the losses of the latter in the exit gas, and, secondly, that the volume of liquid in circulation in the system is very small, a considerable advantage when fire risks are taken into account. In a patent of addition to the above (G.P 469170, 1927) the crude carbon disulphide is first warmed and led into a sulphur separator prior to distillation, while further addition patents (G.P. 485770, 1927, and 495098, 1928) claim distilling the carbon disulphide from water or a non solvent for sulphur, which separates in the still and is recovered, or from an alkaline or alkaline earth sulphide solution which retains the hydrogen sulphide.

(*b*) Treatment of the Exit Gases from the Plant.

The gases leaving the plant consist of small quantities of inerts (nitrogen, carbon monoxide, etc) together with a high percentage of hydrogen sulphide and appreciable amounts of carbon disulphide carried away on account of its high vapour pressure These gases must be treated first for removal of carbon disulphide, and then for recovery of sulphur from the hydrogen sulphide. The method in general use from early days for carbon disulphide recovery has been to scrub the gas in a packed tower with a non-volatile mineral oil, in which the carbon disulphide is readily soluble, followed by steam distillation of the oil to recover the dissolved disulphide.

Other possible methods of recovery are by adsorption by active charcoal or silica gel (Nicolardot, F.P. 631033); by refrigeration to a low temperature at which the vapour pressure of carbon disulphide becomes very small, and by chemical means (Strossacker, Jones, and Dow Chem. Co, U.S.P. 1768803, 1771384 1930), *e.g.* by caustic alkali or alkali sulphide solutions from which the carbon disulphide can be recovered by distillation. Recovery of the sulphur from the residual hydrogen sulphide takes place either by burning with air in a Claus kiln from which the sulphur is recovered as flowers of sulphur (*cf.* Zahn & Co., B.P. 261990; G.P. 433587, 1925), or by treatment with sulphur dioxide gas, when the sulphur is precipitated, as proposed by Oehme (G.P. 483286), and Vogel and Brown Chem. Co., U.S.A. (U.S.P. 1765809, 1929).

An apparatus suitable for the automatic detection and control of sulphuretted hydrogen which depends on the formation of black lead sulphide and the effect of this on a photoelectric cell has been described by Roberts and Minors (J.S C.I. 1934, 53, 526) and is known to give very satisfactory results in detecting escape of this noxious gas into the atmosphere.

Storage, Handling and Transport of Carbon Disulphide.

On account of the great volatility of carbon disulphide, together with the extraordinary degree of inflammability of its vapour, very special precautions have to be taken in handling it, either in the works or during transport.

Since the liquid is only very slightly soluble in, and considerably heavier ($d_4^{20}=1\ 270$) than water, a protecting layer of water is the simplest method of decreasing evaporation losses, and in all modern plants movement of the liquid in and out of tanks, etc., is effected by water pressure, and the final distilled product is stored under water prior to packing into containers. Pumping the liquid is not safe owing to the danger of sparks and the possibility of gas locking in the pump if the temperature rises or the pressure falls.

For the same reasons as above, when opening up any section of a carbon disulphide plant for cleaning or repairs, rigid care must be taken to ensure that all containers, pipes, condensers, etc., have been thoroughly purged of the vapour by an inert gas (CO_2, N_2, etc.) before air is admitted to the system, and, similarly, before restarting a section of plant which has been opened to atmosphere, the system should be ventilated with inert gas until the oxygen content of the issuing gas is down to less than 1%. No naked lights should ever be allowed in places where carbon disulphide is handled, and during operation rigid care must be taken to ensure that the whole plant always works under a slight positive pressure in order that no possibility exists of air being drawn in from outside through leaking joints, lutes, etc. An interesting paper on methods of combatting carbon disulphide fires appeared in Chem. Met. Eng. 1927, 34, 83, in which it is shown that the best and most efficient extinguisher is water, added gently, without splashing, to the burning liquid, so that it rises slowly to the surface, and forms a non-inflammable layer. Foam extinguishers and water sprays cause splashing of the carbon disulphide and are often ineffective, while carbon tetrachloride is not successful until used in quantities greater than that of the carbon disulphide. Carbon disulphide vapour is electrically sensitive to a very high degree, and all containers, pipes, etc., with which the vapour comes into contact must be efficiently earthed to prevent the accumulation of electrostatic charges which might give rise to ignition of the vapour. It is also highly toxic, inhalation of the vapour producing giddiness, vomiting, and coma. After prolonged exposure, even in very dilute concentrations, it produces serious effects on the

nervous system. It should, therefore, never be used in a confined space, *e.g.* all packing of carbon disulphide from stock tanks into containers should be done in the open air, and any room or shed in which the material is handled in bulk, *e.g.* in artificial silk factories, must be provided with an efficient draughting system which is capable of picking up the heavy vapour from the floor of the shed and discharging it outside. The transport of carbon disulphide is subject to the provisions of Statutory Rules and Orders, No. 583 (1935), issued by the Home Office, in which specifications for different sizes of containers are detailed. The package in general use is a 50-gallon mild steel drum with dished ends and two rolling hoops to protect the drum from damage. All drums are filled by weight, and have a $7\frac{1}{2}\%$ air space when filled to allow for expansion, and are tested hydraulically to 20 lb. per sq. in. in order to ensure that they are in sound condition.

Physical and Chemical Properties.

Carbon disulphide is a colourless and extremely volatile liquid; the commercial product has a pungent and fœtid smell, but when purified it has a sweet ethereal odour and an acrid taste.

The following summarised figures give recent data on the important physical properties.

Freezing-point.—111·6°C. (Timmermans, Bull. Soc. chim. Belg. 1934, **43**, 626).

Boiling-point.—46·25°C./760 mm. (von Unruh, Z. anorg. Chem. 1902, **32**, 407); 46·25°C./760 mm. (Timmermans, Bull. Soc. chim. Belg. 1924, **24**, 244); 46·27°C./760 mm. (Mathews, J. Amer. Chem. Soc. 1926, **48**, 562).

Vapour Pressure.—(mm. Hg/°C.) 128·39/0, 198·01/10, 296·48/20, 432·76/30, 616·75/40, 859·49/50, 1172·9/60, 2062·1/80 (Mellor, "Inorganic and Theoretical Chemistry," Vol. VI, p. 100, Lond. 1925).

Latent Heat of Vaporisation.—6·60 kg.-cal./mol. (Faust, Z. physikal. Chem. 1924, **113**, 482).

Specific Heat.—0·2296/0°C., 0·239/30°C., 0·249/60°C., 0·2616/100°C., 0·288/160°C. (Hirn, Ann. Chim. Phys. 1867, [iv], **10**, 32).

The molecular heat of carbon disulphide vapour has been calculated from spectroscopic data by Bryant (Ind. Eng. Chem. 1933, **25**, 609) and is expressed by the following formula:—

$$C_p = 9{\cdot}76 + 0{\cdot}0006102T + 0{\cdot}000001894T^2.$$

The error is estimated at less than 5% below 400°C. and 2% between 400° and 2,000° abs.

Density.—1·29215/0°–4°C. (Thorpe, J.C.S. 1880, **37**, 364); 1·2909/1·5°C., 1·2594/23°C., 1·2494/30°C. (Gladstone, J.C.S. 1891, **59**, 291); 1·2661/20°C. (Haagen, Ann. Physik. 1867, **131**, 121); 1·2209/46·25°C. (von Unruh, Z. anorg. Chem. 1902, **32**, 407).

Vapour Density.—2·67 (air=1) at N.T.P. (V. Meyer and C. Meyer, Ber. 1878, **11**, 2257).

Heat of Formation.—26,010 g.-cal./mol. as vapour at constant pressure from amorphous carbon and solid rhombic sulphur (Thomsen, Ber. 1883, **16**, 2616); —22,100 g.-cal./mol. from carbon and solid sulphur (Berthelot, Ann. Chim. Phys. 1881 (5), **23**, 209); and +12,500 g.-cal./mol. as vapour from carbon and sulphur vapour (Koref, Z. anorg. Chem. 1910, **66**, 73).

Solubility of Water in Carbon Disulphide.—(g. per 100 g. H_2O) —0·010/25°C., 0·011/26°C., 0·012/27°C. (Clifford, Ind. Eng. Chem. 1921, **13**, 628).

Adsorption of Carbon Disulphide Vapour by Carbon.—Coolidge (J. Amer. Chem. Soc. 1902, **24**, 1146; 1924, **46**, 596); Schmidt and Hinteler (Z. physikal Chem. 1916, **91**, 103); Tryhorn and Wyatt (Trans. Faraday Soc. 1927, **22**, 134). Heat of adsorption on carbon, 9,650 cals./g. mol., (Miga, J. Chem. Russ. 1935, **5**, 197).

Adsorption by Alumina Gel.—Perry (J. Physical Chem. 1925, **29**, 1462).

The equilibrium of the formation of carbon disulphide from amorphous carbon and sulphur vapour was studied by Koref (Z. anorg. Chem. 1910, **66**, 73) by the streaming method of Nernst in the temperature range 800°–1,100°. His values for the equilibrium constant,

$$K = \frac{(S_2)}{(CS_2)},$$

are as follows: $7{\cdot}8\times10^{-2}$ at 823°C., $11{\cdot}5\times10^{-2}$ at 906°C., $17{\cdot}9\times10^{-2}$ at 1,009°C., $25{\cdot}8\times10^{-2}$ at 1,110°C., from which the heat of formation of carbon disulphide from carbon and sulphur vapour was calculated by means of the Van't Hoff isochore to be +12,500 g.-cal./mol. CS_2. The exothermic nature of the carbon disulphide reaction at high temperatures was thus established, and the discrepancy between this and Thomsen and Berthelot's early values from liquid sulphur was ascribed to the high latent and specific heat of sulphur vapour. This point has already been stressed in connection with the manufacture of carbon disulphide.

On account of the known dangers attending handling of carbon disulphide due to its inflammability, considerable work has been done on limits of inflammability and ignition temperatures of the vapour with air. Le Chatelier and Boudouard (Compt. rend. 1898, **126**, 1512) showed that a concentration of 0·063 g. per litre of air was inflammable; Kubierschky (Z. angew. Chem. 1901, **15**, 129) determined limits from 4% CS_2 to saturation point; Berl and Fischer (Z. Elektrochem. 1924, **30**, 29) in a glass bulb 27 mm. diameter found 2·22–31·2%, in a glass bulb 18 mm. diameter, 2·69–30·2%, in an iron vessel at room temperature, 3·38–29·2% CS_2; A. G. White (J.C.S. 1922, **121**, 1244), 1·06–50% for upward propagation, and 1·91–35·0% CS_2 for downward propagation. For the effect of other vapours on the limits of inflammability, *cf.* A. G. White (J.C.S. 1927, 793). Ignition temperatures vary considerably according to the concentration of carbon disulphide vapour in the mixture, but under certain conditions ignition can occur well below 100°C., which indicates the great danger involved in handling carbon disulphide. Dixon and Russell (J.C.S. 1899, **75**, 600) reported an ignition temperature of 200°C.; Tizard and Pye (Phil. Mag. 1922, **44**, 79) gave 253°C.; and Dixon (Rec. trav. chim. 1925, **44**, 305) found variations from 120°–150°C.; Wartenburg and Kannenburg (Z. physikal. Chem. 1923, **105**, 205) gave 236°C. In the presence of excess oxygen, violent detonation occurs, the highest velocity of detonation observed being 2,640 m. per sec. with the

mixture CS_2+6O_2, and the products of combustion are sulphur and carbon dioxide with traces of carbon oxysulphide. In a deficiency of oxygen, carbon monoxide, free sulphur, and unchanged carbon disulphide occur in the combustion products. If moist air is used hydrogen sulphide is formed (Tizard and Pye (*l c.*)).

Reduction of carbon disulphide with nascent hydrogen (zinc and hydrochloric acid) gives thioformaldehyde $(CH_2S)_3$ (Gérard, Compt. rend. 1856, 43, 396), and passage with hydrogen over heated nickel forms mercaptan like compounds (Mittasch, J. pr. Chem. 1903, [ii], 68, 103) Evans and Stanier (Proc. Roy. Soc. 1924, A, 105, 626) examined the reduction with hydrogen on nickel catalysts.

Carbon disulphide reacts with water under pressure (Schutzenberger, Bull. Soc. Chim 1876, 25, 146) to form indefinite compounds of hydrogen sulphide and carbon disulphide which decompose at 130°C. reforming the components At higher temperatures carbon disulphide and water give rise to carbon oxysulphide, while at 400°–500°C. carbon dioxide and hydrogen sulphide are formed.

Reaction with aqueous alkali forms a mixture of carbonate and thiocarbonate, while alcoholic solutions of alkalis dissolve carbon disulphide readily, giving rise to the important compounds known as *xanthates*,

$$CS_2+AOH+ROH \rightarrow S.C(OR)SA+H_2O$$

A = Alkali metal.
R = Alkyl group.

An important use of the xanthates lies in the domain of metallurgy for the flotation of certain metal sulphides from ores containing them, but the main significance of the xanthate reaction lies in the preparation of viscose, which is the sodium salt of cellulose xanthate, and is prepared by action of carbon disulphide on alkali cellulose.

Chlorination of carbon disulphide is an important industrial reaction, as it forms the basis of the technical manufacture of carbon tetrachloride. For details of this process, *see* CARBON TETRACHLORIDE.

The action of carbon disulphide on metals gives rise to carbon and metallic sulphides, *e g* magnesium (Schonn, Z anal Chem. 1869, 8, 398); mercury (von Bolton, Z. Elektrochem. 1910, 16, 667; Tammann, Z. anorg. Chem. 1921, 115, 145); copper (Schwarz, Dingl. poly. J. 1869, 191, 399); iron and copper (Merz and Weith, Ann. d. Chem. 1868, 514). For miscellaneous reactions, *see* Cavazzi (Gazzetta, 1887, 17, 577), Mylius and Huttner (Z. anorg. Chem. 1916, 95, 257)

The B.S S. for carbon disulphide (No. 662 of 1936) requires $d^{15.5}_{15.5}$ 1·270–1·274, distillation $\nless$95% below 46 4°/760 mm.

A full description of the chemical reactions of carbon disulphide is given by Kausch (op. cit., pp. 26–62).

USES OF CARBON DISULPHIDE.

The major uses of carbon disulphide have altered very considerably in recent years for several reasons. In the first place, the rapid rise of the viscose artificial silk industry has caused a very great increase in the consumption of carbon disulphide, which has, however, been offset to a large extent by its decline from favour as a solvent, owing to its toxicity and inflammability. The solvent properties of carbon disulphide are shared by two other compounds, carbon tetrachloride and trichlorethylene, and since the latter are non-inflammable, and trichlorethylene is less toxic, many of the solvent processes, *e g* the extraction of grease, oils, fats, waxes, etc, no longer employ carbon disulphide but use the less dangerous chlorinated compounds of carbon.

Carbon disulphide finds considerable application in the rubber industry as solvent in the cold vulcanisation process, and as solvent in the process of water-proofing fabrics. It is also used as the starting-point for the manufacture of carbon tetrachloride by the chlorination process (*see* under CARBON TETRACHLORIDE), as a fumigant, and in the manufacture of xanthates which are used in the flotation of ores.

(*a*) *The Manufacture of Viscose Silk.*—By far the greatest quantities of carbon disulphide produced to day are used for the manufacture of viscose by the action of carbon disulphide and caustic soda on cellulose, a reaction discovered by Cross, Bevan, and Beadle in 1892, who obtained a viscous orange-yellow mass. Wood cellulose is used as the raw material, obtained from pine or fir wood by chemical purification using bisulphite solution under pressure. This pre treatment of the wood dissolves out the non cellulosic materials, and leaves a mass of fibrous particles consisting chiefly of α cellulose, which is then bleached by the usual means. It is then treated with 18% caustic soda solution (mercerisation), when the α-cellulose combines with the alkali to form alkali cellulose.

The sheets of alkali cellulose are then pressed and shredded by special machines, and finally left to mature for 2–3 days at a temperature of approximately 25°C. The changes undergone during the maturing process are not known completely, but probably involve some degradation in the cellulose molecule.

The carbon disulphide reaction now takes place in a revolving horizontal mixer provided with cooling arrangements to remove the heat of reaction, the matured alkali cellulose being charged into the mixer, and carbon disulphide in measured quantity run in, the temperature being maintained below 28°C. for 2–3 hours, after which absorption is completed; 2–3% of unabsorbed carbon disulphide is removed by an air blast.

The product consists of a dark orange yellow spongy mass of sodium cellulose xanthate, $S\,C(SNa)O{\cdot}C_6H_9O_4$, which is next dissolved in 3–4% caustic solution, and left to mature at 15°C. for 2–5 days with frequent filtration, before spinning. The colour of crude viscose is ascribed to the presence of sulphur impurities, *e.g.* sodium trithiocarbonate, formed by the reaction between the excess of caustic soda and carbon disulphide according to the equation,

$$3CS_2+6NaOH=2NaCS_3+Na_2CO_3+3H_2O$$

together with sulphides and polysulphides, etc. These impurities are, however, decomposed during spinning by the sulphuric acid in the coagulating bath with evolution of hydrogen sulphide, which must be removed by efficient ventilation.

According to theory, 100 kg. of chemically pure alkali cellulose require 24·7 kg. of caustic soda, and 46·9 kg. of carbon disulphide; in actual practice, however, this theoretical quantity of carbon disulphide is never used, the usual quantity being only 31–33 kg. of carbon disulphide per 100 kg. of pulp. For full description of the use of carbon disulphide in the viscose silk industry, *see* Kausch (*op. cit.*, pp. 167–179) and also the monograph "Artificial Silk," by Reinthaler (translated by Rowe), published by Chapman and Hall (1928).

(*b*) *Carbon Disulphide as a Solvent.*—From the early days of production carbon disulphide was used in large quantities for the extraction of oils, fats, and grease from a variety of commodities, but it has now been almost entirely replaced for this purpose by trichlorethylene.

As a matter of historical interest, Deiss (Dingl. poly. J. 1857, **146**, 433; 1861, **159**, 436; 1863, **170**, 290; G.P. 13252, 46015) described the method of extraction of fatty oils from seeds, oil cakes, also other pressed residues on a large scale, in which 25 tons of oil cake when treated with carbon disulphide, gave 2½ tons of vegetable oil in a 30 hours cycle.

The use of carbon disulphide as solvent persists in certain parts of Europe to-day, *e.g.* in Spain, where it is used for extracting olive oil from the pressed residues of olives. Bohle (Chem.-Ztg. 1924, **48**, 745, 785; *ibid.* 1931, **55**, 981), Caddick (Chem. Age, 1928, **19**, 536), Anon. (Chem. Trade J. 1932, **91**, 398) described the method in use in which the pressed residues ("Orujo") are extracted in large iron cylinders 8 ft. diameter by 15 ft. high, holding 7 tons of orujo, by means of carbon disulphide, 10 tons of which per charge are forced into the cylinder at the bottom, and allowed to digest for two hours. Two cylinders are used in series, the partly saturated disulphide passing counter-current to the incoming residues. Four extractions are necessary on each charge of residues in order to remove the oil. The solution of oil in disulphide is passed to steam-heated Lancashire boilers in which the solvent is distilled off and returned to the system. The quantities of oil extracted from the charge are 700, 170, 80, 50 kg. during each of the four washes respectively, and the final residues contain 2·5% of oil compared with 10·27% on entering the extractors. Losses of carbon disulphide are only 0·1% of that used, but Bohle states that transport difficulties are so great during summer in South Spain that trichlorethylene is being seriously considered as an alternative in spite of its higher price.

Greece imported, in 1926, 900 tons of carbon disulphide for the extraction of oil from residues, 529 tons being obtained from France, and 371 tons from Italy (Chem. Trade J. 1928, **83**, 192).

(*c*) *Carbon Disulphide in the Rubber Industry.*—The earliest patent on the use of carbon disulphide in the cold vulcanisation of rubber was that of Parkes (B.P. 11147, 1846), in which a solution of sulphur chloride in the solvent was used. This was followed by patents of Forster and Hartfield (B.P. 3215, 1868) and Forster (B.P. 1532, 1877). The process using carbon disulphide as solvent has been developed considerably. Conillardon (F.P. 384061) uses a solution of sulphur chloride in carbon disulphide which is saturated with sulphur; Le Blanc and Kröger (G.P. 408306, 409214) a solution of sulphur thiocyanate in carbon disulphide; Catalpa Ltd. (B.P 170682; G.P. 411522) use organic bases and a filler with carbon disulphide as solvent; Naugatuck Chem. Co., Connecticut (F.P. 561819, 587933) use carbon disulphide with a mixture of inorganic compounds and amines, *e.g.* 100 parts rubber, 10 parts zinc oxide, 3 parts sulphur, 5 parts benzylamine, 5 parts carbon disulphide, left at 100°–140°C. for 48 hours. Other patents on this subject are U.S.P. 1537865, 1551042, 1574676 (Miller Rubber Co.), and U.S.P. 1521739 (Dovan Chem. Corp., Wilmington), which deal with vulcanisation accelerators.

(*d*) *The Manufacture of Xanthates.*—Xanthates are readily prepared from the alcohol, carbon disulphide, and caustic soda. The latter is dissolved in the alcohol in an agitator, and the mixture cooled to room temperature, when carbon disulphide is added at such a rate as to keep the temperature at 20°–30°C. until reaction is complete, in about 4–7 hours. After distillation of any unchanged carbon disulphide and alcohol, the powdered xanthate is dried *in vacuo* and packed for sale. The reaction is shown in the following equation:—

$$CS_2 + NaOH + EtOH = S{:}C\begin{matrix} \diagup OEt \\ \\ \diagdown SNa \end{matrix} + H_2O$$

Sodium ethyl xanthate.

British Dyestuffs Corporation (B.P. 292500) use the straightforward reaction described above, whilst a modification is described in U.S.P. 1559504 (Crowell and Breckinridge, California) in which an inert solvent such as toluene or kerosene is used. The mixture of caustic soda and alcohol in the solvent reacts almost quantitatively with carbon disulphide to form xanthates. The toluene is distilled off in vacuo and takes the water with it which facilitates drying.

U.S.P. 1591723 adds a mixture of carbon disulphide and alcohol to solid caustic soda, whilst the Great Western Electro-Chemical Co. California, in U.S.P. 1636229, carry out the reaction in contact with a chlorinated hydrocarbon (*e.g.* carbon tetrachloride, trichlorethylene, etc.). A further patent of the latter firm (U.S.P. 1606573) covers the production of dixanthates by an electrolytic process. The most important use of xanthates is in the manufacture of viscose silk; other uses are in connection with the flotation of ores and the vulcanisation of rubber. It is also used as a fungicide.

(e) *Carbon Disulphide as Fumigant.*—The toxic properties of carbon disulphide were early applied for fumigation purposes, and large quantities of the substance were used in vineyards all over Europe for destroying the vine-louse (*Phylloxera*), the plants at Swozowice and Zalatna, Austria-Hungary, described previously, being built specially in order to provide supplies of carbon disulphide for this purpose.

Various mixtures of carbon disulphide have been used for fumigation, *e g.* with pyridine and nitrobenzene (G P. 343865, 346643); with potassium thiocarbonate; with carbon tetrachloride, and monochlorbenzene (Aust P. 94342), emulsions with water, etc

Other uses in fumigation are in the control of various insect pests, and extermination of vermin, such as mice, rats, rabbits, etc. A lengthy description of the uses of carbon disulphide for fumigation will be found in Kausch (*op. cit*, pp. 154–161)

Statistics.—Production statistics in respect of the chief manufacturing countries are not available in a detailed form for a number of reasons, but very illuminating figures in respect of the international trade in carbon disulphide are given in an article in Chem Trade J. 1937, **101**, 250.

World production of carbon disulphide increased from 110,000 to 260,000 tons per annum between 1929 and 1936, more than 80% of this total being employed in the production of artificial fibres, based on cellulose xanthate as an intermediate stage. It is probable that almost 90% of the world output of carbon bisulphide is produced in six countries, viz Germany, Japan, U S A, Italy, United Kingdom, and France.

An approximate estimate of current production in the United Kingdom is between 25,000, and 30,000 tons, an additional 500–1,000 tons per annum being imported

Details of import and export trade for the majority of European countries and certain American and Asiatic countries are also given in the article referred to above. F. R

CARBON MONOXIDE.

Occurrence.—Carbon monoxide is present in the atmosphere of industrial towns, its content often being 5 parts per million of air. Its presence is due to incomplete combustion in industrial and domestic fires, furnaces, and in internal combustion engines. The carbon monoxide content in a garage may be still higher, and in a large garage its concentration in the air has been found to be 164 parts per million with a momentarily amount of 890 parts per million (Katz and Frevert, Ind. Eng. Chem. 1928, **30**, 31). The exhaust gases from motor vehicles contain up to 12% carbon monoxide, high figures being obtained because the carburettors are normally set for maximum power and not for economy. In any case, some carbon monoxide is, in practice, certain to be present. The ventilation of the atmosphere in tunnels carrying motor traffic is therefore of considerable importance.

Tobacco smoke also contains some carbon monoxide, and according to Armstrong and Evans (Brit. Med. J. 1922, I, 992) cigarette smoke contains 0 6–0 9% carbon monoxide, smoke from pipes 0 7–1·1%, and that from cigars 6–8% when smoked quickly. The rate of smoking and the closeness of the packing of the tobacco are the chief factors.

Even with a well aerated Bunsen flame burning coal gas, the carbon monoxide content of the products of combustion is as high as 31 parts per million in the undiluted dry products, and in a poorly aerated flame, 44 parts; in the combustion products of a luminous flame, the quantity falls to 13 parts per million (Davies and Hartley, J.S C.I. 1927, **46**, 201T). The results of the determination of the small quantities of carbon monoxide produced when burning coal gas in normal domestic gas appliances is given in various reports by the Gas Investigations Committee of the Institution of Gas Engineers (*see* Gas J. 1928, **182**, 880).

The gases in street manholes have been found to contain large quantities of carbon monoxide, in some cases more than 0 1% (Katz, Meiter, and Bloomfield, U.S. Bur. Mines, Rept. Invest. No. 2710, 1925)

Gases from coal mines also contain carbon monoxide resulting from partial combustion of coal, from the products of combustion of the explosives used in mining the coal, and as the result of "fire damp" explosions—the gas containing the carbon monoxide is then spoken of as "after damp." During the war, poisoning by carbon monoxide, resulting from the explosion of propellant and high explosives, became serious, since dangerously high concentrations were liable to be found in naval gun turrets, machine gun emplacements, pill boxes, tanks, etc., and as a result of mining and sapping operations. Respirators were devised to deal with these situations.

Carbon monoxide is also formed by the action of oxygen on certain organic substances such as pyrogallol, and for this reason precautions must be taken when using this reagent for the determination of oxygen in a gas mixture.

Production.—Carbon monoxide is produced by the partial oxidation by oxygen, air, or steam, of organic materials and particularly carbon, at high temperatures; by reduction of carbon dioxide by hydrogen, carbon, or certain metals, at high temperatures; by the reduction of some metallic oxides or carbonates with carbon, and in the manufacture of carbide. It is also formed by heating various organic compounds alone or with concentrated sulphuric acid. The simplest method of preparing carbon monoxide is by the action of concentrated sulphuric acid upon formic acid. The gas evolved should be passed through caustic soda solution to remove any carbon dioxide or sulphur dioxide formed during the reaction.

Carbon monoxide is seldom made in the pure state, its most important industrial form being in admixture with hydrogen, etc, in water gas and producer gas.

The destructive distillation of coal results in a good deal of the oxygen present in the coal appearing as carbon monoxide in the resultant gas, the quantity depending on the composition of the coal used, and the carbonising conditions. With vertical and horizontal retorts using a gas

coal, the carbon monoxide content is about 8–10%, and if the latter retorts are "steamed" the carbon monoxide content rises to about 18% owing to the formation of water gas. When carbonisation is carried out in modern coke ovens, the carbon monoxide content of the gas is about 6%.

Blue water gas, made for addition to coal gas and for hydrogen manufacture, contains about 40% carbon monoxide, the blow gas made by blowing air through the coke bed before steam is admitted, containing from 5–10% carbon monoxide, depending on the rate at which the air is blown and on the temperature of the water gas generator. Carburetted water gas, which is blue water gas to which is added the products of the cracking of a petroleum oil, contains about 30% carbon monoxide, depending on the operating conditions.

Producer gas, made by blowing simultaneously air and steam through a red hot coal bed, and which is used for firing furnaces, contains about 30% carbon monoxide, while suction gas, which is producer gas made from coke, contains about 25–30% carbon monoxide, is used for furnace firing, driving gas engines, and ammonia manufacture.

Blast-furnace gas which results from the reduction of iron oxide by red hot coke through which air is blown, contains about 27–30% carbon monoxide and is used for driving gas engines and steam raising.

Carbon monoxide of considerable purity can be obtained by passing carbon dioxide through charcoal or coke at a temperature not lower than 1,000°C., but if continuous operation is required, oxygen must be added to supply the heat removed by the decomposition of the carbon dioxide. The gases will invariably contain some carbon dioxide, the amount depending on the temperature of the fire bed and the rate at which the carbon dioxide is blown through, and this can be washed out with an alkaline carbonate solution which can be subsequently heated to decompose the bicarbonate formed. Nitrogen from the air and hydrogen from the decomposition of any water in the coke or carbon dioxide will also be present.

Relatively pure carbon monoxide is also obtained from water gas when the Linde-Frank-Caro liquefaction process is employed for the separation of the gases, the carbon monoxide being separated as liquid. It is also obtained, mixed with a little hydrogen and nitrogen, when small quantities of carbon monoxide present in ammonia synthesis gases are removed by scrubbing with ammoniacal copper solutions under pressure. When the pressure on the liquid is reduced or the liquid heated, the carbon monoxide it contains is evolved in a relatively pure form.

The use of ammoniacal cuprous solutions for the removal of carbon monoxide industrially has been studied by Gump and Ernst (Ind. Eng. Chem. 1930, 22, 382) who concluded that an ammoniacal cuprous lactate solution, made from cuprous oxide, lactic acid and ammonia gas, was the best for this purpose. At 0°C. the solution absorbed 12–15 times its own volume of carbon monoxide and when regenerated by heating to 60°C. gave a gas containing 97–99% carbon monoxide, with hydrogen and nitrogen as impurities. No copper was precipitated from the solution as is likely when formate or carbonate solutions are used.

Carbon monoxide–hydrogen mixtures can be obtained from gases containing methane by the action of steam or carbon dioxide under the influence of a catalyst (*see* Reactions with Hydrogen).

PROPERTIES.—Carbon monoxide is a colourless gas with, according to some, a metallic odour and taste. Its critical temperature is −139°C., critical pressure 34·6 atm., and its critical density 0·311 g. per c.c. Its boiling-point is −190°C. and melting-point −207°C. The density of the gas at 0°C. and 760 mm. Hg is 1·250 g. per litre, and compared with oxygen, $O_2=1$, is 0·8749.

The following figures for the vapour pressure of the liquid are given in "International Critical Tables," 1928.

p atm. .	1	6·7	20·9	35
t°C. . .	−192	−170	−150	−139

The determination of its specific heat at high temperatures is rendered difficult by its dissociation into carbon dioxide and free carbon, and from a review of the literature, Partington and Shilling, "The Specific Heat of Gases," 1924, give, for the true molecular heat at constant volume, in cals. per g. mol., the following equation :

$$C_v=4{\cdot}970+0{\cdot}00017t+3{\cdot}1\times10^{-7}t^2$$

The values for C_p-C_v at 0°C. and 20°C. are 1·999 and 1·997 respectively and the ratio C_p/C_v at 0°C. is 1·407 (Schweikert, Ann. Physik, 1915, [iv], 48, 593 ; 1916, [iv], 49, 433).

Carbon monoxide is slightly soluble in water. The volume of gas at 0°C. and 760 mm. Hg dissolved by 1 vol. of water when the pressure of the gas, excluding that of the water vapour, is 760 mm., is given below (Seidell, "Solubility of Inorganic and Organic Substances," 1919).

t°C. . .	0	20	40	60
Vol. gas.	0·0354	0·0232	0·0178	0·0149

At 19°C. under a pressure of 900 mm. Hg the volume of gas dissolved is 0·025 c.c. (S.T.P.) and at 8,000 mm. Hg 0·024 c.c. (Cassuto, Physikal. Z. 1904, 5, 233).

Carbon monoxide is adsorbed by wood charcoal to a small extent (*see* Homfray, Proc. Roy. Soc. 1910, 84, A, 99).

The molecular heat of formation from graphite at constant pressure and 18°C. is 26,400 g. cals. ("International Critical Tables," 1931), and the molecular heat of combustion at constant pressure and 25°C. is 67,623±30 g. cals. (Rossini, *Bur. Stand. J. Res. 1931*, 6, 37).

Carbon monoxide decomposes to carbon dioxide and carbon at moderate temperatures when in contact with firebricks which contain ferric oxide. The deposition of carbon is thought to cause the disintegration of firebricks of this type in coke ovens, etc. The promotion of carbon monoxide dissociation by various firebricks at 700°C. and lower has been investigated by Hubbard and Rees (Trans. Ceram. Soc.

1929, 28, 277), who found that various fire-bricks, alumina, clay, ferric oxide, etc., promoted the dissociation at temperatures as low as 260°–300°C. and that the ferric oxide content of the refractory should be reduced to avoid this reaction.

The oxidation of carbon monoxide by sulphates has been described by Wehmer (Ber. 1926, 59, [B], 887) who found that carbon monoxide was removed from towns gas when this was incubated with soil. The action is due to soil microflora, the oxygen required being supplied by the sulphates present in the soil.

TOXIC EFFECTS.—When inhaled, carbon monoxide combines with the hæmoglobin of the blood to the exclusion of oxygen and, if it were not for this, it would be classed with hydrogen and nitrogen as a simple asphyxiant. The result of this combination is that, when the concentration of carbon monoxide is sufficiently high, persons inhaling it collapse owing to the non functioning of the blood. There are no chronic after-effects when once the patient has recovered.

The effect of carbon monoxide on plants is variable, sometimes being toxic and at others inert, but animals whose blood contains no hæmoglobin are normal in an atmosphere of 80% carbon monoxide, 20% oxygen (*see* Miller, "Plant Physiology," 1931; and Henderson and Haggard, "Noxious Gases," 1927).

The reaction between carbon monoxide and hæmoglobin is a reversible one

$$RO_2 + CO \rightleftharpoons RCO + O_2$$

(where R represents a molecule of hæmoglobin), so that on breathing air or oxygen, the carbon monoxide is displaced.

All the carbon monoxide inhaled does not combine with the blood and it has been found that in an atmosphere containing up to 0.114% carbon monoxide, if no work is done, a maximum of 40% of the amount inhaled will be absorbed, *if work is done, the amount increases to 45%* (Veale, Iron and Coal Trades Review, 1922, 104, 936). Combination of carbon monoxide with hemoglobin takes place more rapidly at the beginning of the exposure and is increased with an increase in temperature. There appears to be a definite relationship between the amount of hæmoglobin, oxygen, carbon monoxide, and the p_H in equilibrium (Stadie and Martin, J. Clin. Research, 1925, 2, 77). An increase in H ion concentration hastens the elimination of carbon monoxide, thus explaining the beneficial results when oxygen containing a little CO_2 is administered to a gassed person.

Small individuals succumb more rapidly to carbon monoxide than larger ones because the volume of their respiration is greater in relation to their volume of blood. Thus mice or canaries succumb to the gas much more readily than does man, and for this reason they are used to detect the presence of dangerous amounts of carbon monoxide in suspected atmospheres. A man can breathe the same atmosphere for about 20 times as long as a mouse or canary before becoming gassed.

The effects of various concentrations of gas are given below (Henderson and Haggard, *l.c.*):

	Parts per million
Allows an exposure of several hours	100
Allows an exposure of 1 hour without appreciable effect	400–500
Appreciable effect after 1 hour	600–700
Unpleasant but not dangerous after 1 hour	1,000–1,200
Dangerous for exposure of 1 hour	1,500–2,000
Fatal in exposures of less than 1 hour	Over 4,000

When breathing an atmosphere containing high carbon monoxide concentrations, the individual collapses with practically no warning (as happens in a small closed garage with a car engine running) but with smaller concentrations a headache makes itself felt.

With regard to the treatment of a gassed person, as carbon monoxide is not oxidised or destroyed by the body but expelled as carbon monoxide, it is important to hasten its elimination. (It has recently been suggested that as a result of continued exposure to small carbon monoxide concentrations, the absorbed carbon monoxide may be removed by some other process.) Mild gassing cases only need a short rest and fresh atmosphere, but in more serious cases, oxygen containing 5% carbon dioxide may be administered—the carbon dioxide, apart from its effect on the p_H, also stimulates lung action. (Oxygen containing 5% carbon dioxide for this purpose is sold in cylinders.) In cases where the patient has collapsed, he should be removed into fresh but not cold air at once, covered with a blanket to keep him warm, and turned on his stomach with his head on one side. If he is breathing, the oxygen carbon dioxide mixture should be administered for 15–30 minutes, and if he is not, artificial respiration should also be carried out. The oxygen-carbon dioxide mixture should be administered for 15–30 minutes after breathing has been resumed. The use of alcohol is inadvisable. The after treatment consists in keeping the patient warm and comfortable to prevent pneumonia.

When work is to be carried out in an atmosphere likely to contain high amounts of carbon monoxide, the men engaged on the work should be provided with a gas mask and, if working in places such as in tanks, should be attached to a life line. The most satisfactory types of mask for general use are face masks to which air is blown through a flexible pipe, the air being blown by a manually driven blower and coming from an uncontaminated source. These masks are simple, foolproof, and only need keeping hygienic, whereas the canister type, which contain a catalyst for the combustion of carbon monoxide with air, will only deal with a limited amount of carbon monoxide and if used on rare occasions, are likely to be less reliable than the simple type. For rescue work, a gas mask used with a small cylinder of oxygen strapped on the wearer's back is practically essential and whenever carbon monoxide is present in industrial gases, a number of these mask oxygens sets should be kept in

strategic positions and a number of men trained in their use.

When it is possible for carbon monoxide to contaminate to an appreciable extent any atmosphere in which men have to work, a test should be made using white mice or canaries, and these should remain with the workmen the whole time. Mice and canaries will give visible indication of gassing long before any harm will come to a human being.

During the war, when the use of the masks indicated was not practicable, various catalysts were made for the oxidation of carbon monoxide to carbon dioxide by atmospheric air. The catalysts were placed in a canister attached to the mask. Among the catalysts were mixtures of copper oxide, manganese peroxide with 1–5% of ceric oxide as promoter, and a mixture, known as *Hopcalite*, of copper oxide 30%, manganese peroxide 50%, cobaltic oxide 15%, and silver oxide 5%. The method of preparation is very detailed, but the catalyst is extraordinarily active, so much so that, if used in air containing 2% carbon monoxide, the heat of reaction is sufficient to necessitate the cooling of the air before it is breathed. The gases are dried with calcium chloride before passing to the catalyst (Rogers, Piggott, Bahlke, and Jennings, J. Amer. Chem. Soc. 1921, **43**, 1973; Merrill and Scalione, *ibid.* 1982; Almquist and Bray, *ibid.* 1923, **45**, 2305; Whitesell and Frazer, *ibid.* 2841; Lamb and Vail, *ibid.* 1925, **47**, 123). Copper oxide and manganese peroxide prepared by suitable methods can also catalyse the combustion of carbon monoxide at 20°C. and 0°C. respectively, and oxides of iron, nickel, cobalt, and silver can also be made to give a measurable reaction at ordinary temperatures.

Carbon monoxide burns in air with a characteristic blue flame and when ignited with air or oxygen gives a relatively slow explosion.

Ignition Temperatures.—The ignition temperature of any given mixture of gases depends on the method employed for igniting the mixture. If, at atmospheric pressure, carbon monoxide is passed into oxygen, both gases being heated to the same temperature before mixing, the carbon monoxide ignites after half a second at 667°C. and after 10 seconds at 645°C. With air in place of oxygen, the temperatures are 696°C. and 668°C. respectively ("International Critical Tables," 1927). By applying an electrically heated wire to mixtures of carbon monoxide and air at atmospheric pressure, McDavid (J.C.S. 1917, **111**, 1003) found that the minimum temperature of the wire which would cause an instantaneous explosion was 931°C. By compressing mixtures adiabatically until ignition took place, and calculating the ignition temperature from the degree of compression, Falk (J. Amer. Chem. Soc. 1906, **28**, 1517; 1907, **29**, 1536) obtained the following ignition temperatures:

$6CO+O_2$	721°C.
$4CO+O_2$	628°C.
$2CO+O_2$	601°C.
$CO+O_2$	624°C.
$2CO+O_2+N_2$	634°C.
$2CO+O_2+2N_2$	685°C.

Mixtures of carbon monoxide and oxygen which are very dry are difficult to ignite, and Bone and Weston (Proc. Roy. Soc. 1926, A, **110**, 620) found the minimum condenser spark energy necessary to ignite a mixture of $2CO+O_2$ was about 30 times greater in the case of a calcium chloride dried mixture than for one saturated with water vapour at 17°C.

Limits of Inflammability.—The limits of inflammability of any given gaseous mixture will depend on the direction in which the flame is moving and on the size of the vessel through which the flame is passing. With mixtures of carbon monoxide and air, containing 1% water for the lower limits and 2% for the upper, contained in glass tubes and ignited by sparking, White (J.C.S. 1924, **125**, 2387) obtained the following figures for the limiting percentages of carbon monoxide in air, outside which the mixture would not propagate flame.

Tube diameter.	Propagation.		
	Upward.	Horizontal.	Downward.
2·5 cm.	13·2–71·0	15·9	16·3–70·0
5·0 „	13·1–72·0	13·1	15·7–70·5
7·5 „	12·8–72·0	13·6	15·3–70·5

The effect of increasing the temperature is to widen the limits, and White (J.C.S. 1921, **127**, 672) found that with a tube 2·5 cm. diameter, the limits for the carbon monoxide concentration in carbon monoxide/air mixture for downward propagation were:

At 100°C.	14·8–73·7
„ 300°C.	12·4–75·0
„ 400°C.	11·4–77·5

The limits also widen when oxygen replaces air and under conditions of downward propagation the limiting percentages of carbon monoxide which for air mixtures were 15·6–70·9 became 16·5 and 93·5 with carbon monoxide-oxygen mixtures (Terres, J. Gasbeleucht. 1920, **63**, 785, 805, 820, 836).

The effect of pressure is considerable. Coward, Cooper, and Jacobs (J.C.S. 1914, **105**, 1069) determined, for different mixtures of carbon monoxide in oxygen, the pressures below which the mixtures would not ignite. The results are:

% CO in O_2.	Pressure, mm. Hg.	% CO in O_2.	Pressure, mm. Hg.
94	>400	40	26
91	99	33	32
80	55	25	74
75	50	20	92
50	30	15	148

A large amount of work on the explosion of different mixtures of carbon monoxide and air and oxygen at high initial pressures has been carried out during the last 15 years or so by Bone and his co-workers, and the original papers should be consulted. An account of his earlier work is given in "Flame and Explosion in Gases," Bone and Townend, 1928. The limits

of inflammability for mixtures of carbon monoxide and air when exploded in a spherical bomb are 16 2–66 3% carbon monoxide at 10 atm. initial pressure, 20 3–57 8 at 50 atm., and 23 1–52 3 at 125 atm.

SPEED OF INITIAL UNIFORM MOVEMENT.—Mixtures of air or oxygen and carbon monoxide, when dried over phosphorus pentoxide, are difficult to ignite and burn slowly, the rate depending on the dryness. The speed of uniform movement of carbon monoxide–air flames during their initial phases in horizontal glass tubes 2 5 cm. diameter has been measured by Chapman (J.C.S. 1921, 119, 1677). With mixtures saturated with water vapour at 12°C. the speed with a mixture containing 20% carbon monoxide is 25 cm. per sec. This increased to a flat maximum of 62–63 cm. per sec. at 45–50% carbon monoxide and decreased to 25 cm. per sec. with 70% carbon monoxide. With oxygen instead of air, these speeds are increased considerably, a mixture containing 50% carbon *monoxide saturated with water vapour at 12 5°C.* having a speed of 144–147 cm. per sec., 60% carbon monoxide a speed of 163–167 cm. per sec., 80% carbon monoxide a speed of 191–195 cm. per sec., and 92 5% carbon monoxide a speed of 51 cm. per sec.

RATES OF EXPLOSION.—The classic work of Dixon published in the "Proceedings of the Royal Society" and the "Philosophical Transactions of the Royal Society of London" before the end of last century and continued since, must be consulted for details on the meaning and determination of the rates of explosion of mixtures containing carbon monoxide. Dixon found that where an explosion wave was set up in $CO-O_2$ mixtures, its speed varied considerably with the water content of the exploding gases. With the mixture $2CO+O_2$ dried over sulphuric acid and phosphorus pentoxide, the speed of the explosion, with the gases initially at atmospheric pressure, was found to be 1,264 m. per sec. With the gases saturated with water vapour at 10°C., the speed was 1,676 m. per sec. A maximum of 1,738 m per sec. was reached with the mixture saturated at 35°C.

Measurements of the pressures developed during the explosion of various mixtures containing carbon monoxide have been used for the *determination of the specific heats of gases* at high temperatures (Pier, Z. Elektrochem. 1910, 16, 897; Bjerrum, Z. physikal Chem. 1912, 79, 537), and a thorough study of explosions of these mixtures at high initial pressures (50 atm. and higher) has been made by Bone and his collaborators and published in the Proc. Roy. Soc. for 1919 and onwards. Bone found that, whilst the maximum explosion pressure of both dry and wet $CO-O_2$ mixtures was relatively slowly reached, the presence of a small amount of hydrogen caused the maximum pressure to be reached much more rapidly.

REACTION WITH CARBON.—For the calculation of the equilibrium constants of a number of fundamental reactions, *see* Saunders, J. Physical Chem. 1924, 28, 1151.

$$2CO \rightleftharpoons CO_2+C$$

The reaction of carbon dioxide with carbon or the dissociation of carbon monoxide is one that has to be considered whenever the temperature of carbon monoxide is raised above about 600°C. Boudouard (Ann. Chim. 1901, [vii], 24, 5) and Rhead and Wheeler (J.C.S. 1910, 97, 2178) studied this reaction and the following table, showing the percentage of carbon dioxide by volume, in equilibrium with carbon (graphite) and carbon monoxide at atmospheric pressure, has been taken from their results.

t°C.	% CO_2	t°C.	% CO_2
600	77	1,000	0 59
700	42	1,100	0 15
800	7	1,200	0 06
900	2·22		

Rhead and Wheeler found that the reaction between carbon dioxide and carbon at 850°C. took place 166 times faster than the carbon monoxide dissociation at the same temperature.

These results explain why carbon monoxide is produced by passing air or carbon dioxide over red hot coke as in the manufacture of producer gas and water gas, and in the blast-furnace, etc., and show that consideration must be given to this reaction whenever processes using either carbon monoxide or carbon dioxide at a high temperature are employed. The nature of the carbon also influences the equilibrium, although at high temperatures the carbon will eventually become graphitised, and the same result will be obtained irrespective of the carbon originally employed (Dent and Cobb, J.C.S. 1929, 1903).

REACTION WITH OXYGEN.—

$$CO+\tfrac{1}{2}O_2=CO_2$$

The dissociation of carbon dioxide into carbon monoxide and oxygen takes place to an appreciable extent only at high temperatures. The table below has been drawn up from measurements made by Nernst and von Wartenburg (Z. physikal. Chem. 1906, 56, 548,) Langmuir (J. Amer. Chem. Soc. 1906, 28, 1357), and Löwenstein (Z. physikal. Chem. 1905, 54, 707).

t°C.	1,100	1,200	1,300	1,550
% CO_2 dissociated	0 014	0 032	0 047	0 4

REACTION WITH STEAM.—

$$H_2+CO_2=H_2O+CO$$

Equilibrium determinations for this reaction have been carried out by Hahn (Z. physikal. Chem. 1903, 44, 513; 1904, 48, 735) who approached the equilibrium from both sides over heated platinum as a catalyst, and by Haber and Richardt (Z. anorg. Chem. 1904, 38, 5) who used flames.

The following figures have been obtained from their results and show how the equilibrium constant at constant pressure varies with the absolute temperature :

$$K_p = \frac{p_{H_2O} \cdot p_{CO}}{p_{H_2} \cdot p_{CO_2}}$$

T°K	800	1,000	1,200	1,400
Kp	c. 0·2	0·65	1·32	2·08
T°K	1,600	1,800	2,000	—
Kp	2·95	3·80	c. 4·7	—

Bryant (Ind. Eng. Chem. 1931, **23**, 1019) discusses the specific heats of the gases involved and the calculation of the free energy and equilibrium constant of this reaction in some detail. He gives the heat of reaction at 298°K. as 9,751 g.-cal. (*see also* Neumann and Köhler, Z. Elektrochem. 1928, **34**, 218).

This reaction is used industrially for the manufacture of hydrogen from gases containing carbon monoxide, usually water gas. Steam, in excess of the requirements of the above equation, is added to water gas and the mixture heated by passage through interchangers by which the gases, after the conversion of carbon monoxide to carbon dioxide are cooled. The heated mixture is then passed through a catalyst, usually an oxide of one of the metals of the iron group, at about 500°C., which converts most of the remaining carbon monoxide to carbon dioxide. The reaction is exothermic, and in order to keep the temperature from rising too high, and so preventing the conversion taking place, since lower temperatures favour the production of hydrogen, some of the heat in the partly converted gases is used to pre-heat the inlet gas mixture. The partly cooled, partly converted mixture is then passed through a second catalyst chamber, where the carbon monoxide content is reduced to about 4–5% depending on the temperature, quantity of excess steam, rate of passage of the gases, and catalyst activity. The gases are then partially cooled by passing through more interchangers where they heat the inlet gas, and are finally cooled by washing with water. When used for ammonia synthesis or hydrogen production, the carbon dioxide is washed out of the mixture with water under pressure (usually 25 atms. or higher), and the remaining carbon monoxide is removed by washing with ammoniacal copper solutions or similar absorbents under higher pressure. The carbon monoxide is recovered from the solution by releasing the pressure or raising the temperature, and passes back to the inlet of the converters. A large number of catalysts have been proposed (most of which have been patented), with and without promoters, but if the catalyst is very active, sulphur compounds have usually to be removed from the gases before conversion. It has been claimed recently that very active sulphur-proof catalysts can be used for the reaction. Among them are magnesium oxide with a promoter from the uranium group (U.S.P. 1866246) or the fused oxide of a metal of the iron group and copper oxide (U.S.P. 1865770).

An experimental plant has been erected on the Continent for the removal of carbon monoxide from towns gas using the reaction

$$CO + H_2O + CaO = CaCO_3 + H_2$$

at 500°–600°C. The organic sulphur compounds are converted to H_2S and the carbon monoxide is reduced to less than 1%. The lime is regenerated at 800°–900°C. in the presence of air. It is very doubtful if this process is practicable (Chim. et Ind. 1930, **24**, 235).

Reactions with Hydrogen.—A remarkable number of different compounds can be obtained from mixtures of carbon monoxide and hydrogen by catalytic action, the products depending on conditions and catalyst.

(*a*) *Methane Formation.*—The simplest reaction is one in which methane is formed:

$$CO + 3H_2 = CH_4 + H_2O$$

The equilibrium constants below are given in "International Critical Tables," 1930.

$$K_p = \frac{p_{CH_4} \cdot p_{H_2O}}{p_{CO} \cdot p^3_{H_2}}$$

T°K	1,133	1,213	1,307	1,325
log Kp	−2·37	−3·09	−4·06	−4·31

The formation of methane is favoured, therefore, by higher pressure and low temperature.

The reverse reaction has been used, under the action of a suitable catalyst, for the production of hydrogen from gases containing methane. Catalysts made from nickel nitrate or nickel nitrate–aluminium nitrate on a refractory support are stated to be satisfactory, temperatures of 900°–1,100°C. at atmospheric pressure giving a maximum conversion with a minimum amount of side reaction. Refractories alone can be used to promote the methane-steam reaction at 1,000°C., but carbon is deposited through the decomposition of carbon monoxide (Hawk, Golden, Storch, and Fieldner, Ind. Eng. Chem. 1932, **24**, 23). The reaction in which carbon dioxide is used in place of steam is also discussed by the same authors, who quote the equilibrium constants of the reverse reaction,

$$CH_4 + CO_2 = 2CO + 2H_2$$

$$K_p = \frac{p^2_{CO} \cdot p^2_{H_2}}{p_{CH_4} \cdot p_{CO_2}}$$

T°K	1,073	1,173	1,273
Kp	195	$2{\cdot}35 \times 10^3$	$1{\cdot}90 \times 10^4$

It appears to be advisable to use sulphur-free gases for these reactions between carbon monoxide and hydrogen although Hawk, Golden, Storch, and Fieldner used a natural gas with a very low sulphur content.

The formation of methane from gases containing hydrogen and carbon monoxide, in order to increase the calorific value of the gas mixture, can be carried out by passing the gases over finely divided nickel at temperatures of about 250°C. Sulphur-free gases must be employed in order that the catalyst shall not be poisoned, and excess hydrogen, or low percentages of carbon monoxide (below 17%) must be used to prevent the deposition of carbon from the reaction

$$2CO = C + CO_2$$

(b) *Methyl Alcohol*—

$$CO+2H_2=CH_3OH$$

$$K_p=\frac{p_{CH_3OH}}{p_{CO}\,p^2_{H_2}}$$

The values for the equilibrium constant of this reaction at different temperatures have been calculated by Kelley (Ind. Eng Chem 1926, 18, 78). The figures given are :

T°K	300	500
K_p	670×10^5	316×10^{-2}
T°K	700	1000
K_p	154×10^{-5}	206×10^{-7}

The reaction is favoured by an increase in pressure and a decrease in temperature (*see also* Kelley, *ibid* 1929, 21, 353).

This reaction is used to a considerable extent in industry, where it is carried out under high pressure, about 200 atms, and at a temperature of 300°–400°C The compressed carbon monoxide-hydrogen mixture is passed through an interchanger, where the gases are heated by the converted gases, and then through a catalyst A conversion of up to 15% is obtained, depending on the conditions and activity of the catalyst, the methyl alcohol in the mixture is separated by cooling in a condenser After separation of the alcohol, the gases are sent back to the conversion chamber In some cases, the gases have been passed through a number of catalyst vessels, the methyl alcohol being separated after each vessel by cooling Pressures as high as 900 atms have been proposed for this reaction

The catalysts used are zinc carbonate and a mixture of zinc and chromium oxides, and in order to avoid the formation of methane, the catalyst vessels, etc, should be lined with metals such as copper, silver, aluminium, or alloys which do not give carbonyls If the temperature is raised above 400°C, methane formation increases, and the production of higher alcohols, ketones, aldehydes, etc, occurs The presence of sulphur compounds in the gas used for making methyl alcohol tends to poison the catalyst, but this is not serious with low sulphur concentrations. A large number of patents have been taken out within recent years in connection with this process (*see* B P 258887, and Cryder and Frolich, Ind. Eng Chem 1929, 21, 867) The use of alkalised iron catalysts under pressure to give higher alcohols has been described by Frolich and Lewis (*ibid.* 1928, 20, 354).

(c) *Hydrocarbons.*—By selecting suitable methods of preparation of special catalysts, Fischer and Tropsch (Brennstoff-Chem., 1926, 7, 97) have made, from hydrogen and carbon monoxide mixtures (water gas) at ordinary pressures, a number of liquid aliphatic hydrocarbons. The temperatures of the reaction need careful control, depending on the catalyst, in order to suppress the formation of methane ; the temperatures used are 150°–300°C. and metals of the iron group have been used as catalysts in addition to mixtures of the oxides of chromium, zinc, and the rare earths. Sulphur compounds must be removed from the gases. This and similar reactions may become very important industrially in the future.

The equilibrium between carbon monoxide, hydrogen, and a number of hydrocarbons and alcohols has been calculated by Smith (Ind. Eng. Chem. 1927, 19, 801)

(d) *Synthol.*—Using mixtures of carbon monoxide with excess hydrogen, and passing the mixture over an alkalised iron catalyst at 400°C. and 150 atm. pressure, Fischer (*see* "Conversion of Coal into Oils," 1925) obtained a mixture which he termed "Synthol," consisting of alcohols up to C_9, ketones, aldehydes, acids up to C_8, and various esters, with a composition C, 69%; H, 12%; O, 18%, of which 37% distilled below 100°C. and 97% below 200°C. The catalyst has a considerable effect on the product, a weak base with the catalyst giving water soluble compounds, and a strong base oily products. *See also* Fischer (Brennstoff Chem. 1935, 16, 1), who summarises the work on this process, including the preparation of the gases and catalysts

(e) *Carboxylation.*—Carbon monoxide can be used to carboxylate methyl alcohol to give acetic acid according to the reaction

$$CH_3OH+CO=CH_3CO\,OH$$

and to give formic acid by causing steam, hydrogen and carbon monoxide to react under suitable conditions These reactions may be important in connection with artificial silk manufacture.

The formation of acetic acid takes place when methyl alcohol and carbon monoxide are allowed to react over acid catalysts such as boric acid, phosphoric acid and phosphomolybdic acid at 100–300 atms. pressure and 300°–400°C. (B.P. 283989) or at 200°–250°C. at ordinary pressure in the presence of methoxides of zinc or aluminium (B P. 264558, 268845).

Sodium formate can be obtained by passing carbon monoxide under pressure over lumps of caustic soda containing a little water at 100°–120°C. Various modifications have been proposed and a number of patents obtained for these reactions.

(*f*) *Miscellaneous Compounds*—A large number of patents have been taken out covering the reactions of carbon monoxide with hydrogen under the influence of catalysts to give various products. The formation of olefines, used for the manufacture of alcohols, by using oxides of cobalt, copper, and manganese as catalysts at 280°–300°C. (B.P. 291867), of formaldehyde using magnesium, zinc, and mixed oxides of magnesium and antimony at 200°–600°C. (B.P. 272,155), of formanilide, etc, by the action of carbon monoxide on primary and secondary arylamines in the presence of sodium methoxide, or hydroxide, and of *iso*butyl and higher alcohols from carbon monoxide and methyl alcohol are examples.

REACTION WITH CHLORINE.—The formation of phosgene used for dyestuffs manufacture and in gas warfare can be carried out by passing a mixture of carbon monoxide and chlorine over platinum sponge at 400°C. The reaction also takes place in sunlight, and on charcoal.

Reduction of Metals.—Carbon monoxide is a strong reducing agent, and will reduce metallic oxides to metals, usually at a lower temperature than will hydrogen. The reducing action of carbon monoxide plays an important part in connection with the production of iron in blast-furnace and in the manufacture of various steels.

In addition, carbon monoxide forms a number of metallic carbonyls by direct action with the metals, and use is made of this property in the production of nickel by the Mond process. Nickel ores, containing nickel, copper, cobalt, iron, etc., are roasted, crushed, and treated with sulphuric acid, so as to concentrate the nickel. The mixture of oxides, containing about 50% nickel, is passed into a chamber with water gas at up to 300°C. when the nickel oxide is reduced to metallic nickel. The temperature must not be high enough to cause the reduction of the iron oxide to metallic iron, since this might give iron carbonyl, which would later decompose and contaminate the nickel. The reduced ore is then treated with a gas rich in carbon monoxide (about 80%) at a lower temperature (50°–100°C.), when some of the nickel is converted to the carbonyl, the gas leaving this section containing about 2% $Ni(CO)_4$. This gas is then passed into a vessel containing small nickel pellets at a temperature of 180°C., when the carbonyl decomposes, depositing its nickel on the small pellets, the gases being re-cycled. If the temperature is above 200°C. carbon deposition from the carbon monoxide is likely to take place and so contaminate the nickel. The nickel pellets are screened, the smaller ones being returned, and the larger ones becoming the finished product. The ore from the " carbonyling " section is returned to the reducing section when it recovers its property of forming carbonyls, while the gas losses in the system are made up by passing the gases from the ore reducing section through hot charcoal.

Iron carbonyl occurs in small quantities (0·0003 g. per 100 litres) in towns gas according to the conditions of the supply mains (Griffith and Holliday, J.S.C.I. 1928, **47**, 311T).

Detection and Analysis.—Small amounts of carbon monoxide can be detected by passing the gas through a dilute solution of palladous chloride or by its action on paper soaked in this solution, when a darker colour is obtained owing to the production of metallic palladium. Various other reducing gases, however, cause this reaction. The reaction of carbon monoxide with blood can also be used by passing the gas through a dilute aqueous solution of blood when, if carbon monoxide is present, the solution will give a characteristic absorption spectrum with two dark absorption bands between the *D* and *E* lines, which do not disappear on the addition of ammonium sulphide.

The quantitative determination is best carried out in the case of gases containing large quantities of carbon monoxide (above about 0·25%) by absorption in an ammoniacal solution of cuprous chloride. If unsaturated gases such as acetylene, ethylene, etc., are present they must be removed before the carbon monoxide is absorbed. The use of copper ammonium lactate in place of the chloride is stated to be an improvement (Gump and Ernst, Ind. Eng. Chem. 1930, **22**, 382). The carbon monoxide in the gas can be burnt to carbon dioxide by exploding with air or oxygen, by passage with air over heated palladium wires, or by combustion over copper oxide ; the carbon dioxide is determined by adsorption in soda-lime, etc., or the contraction in volume can be measured. In connection with this method, a good deal of work has been carried out on the oxidation of carbon monoxide only, in the presence of hydrogen, Hopcalite being found to oxidise the carbon monoxide in mixtures of hydrogen, carbon monoxide, and air without burning the hydrogen, so long as the percentage of carbon monoxide does not exceed 1% (Lamb, Scalione, and Edgar, J. Amer. Chem. Soc. 1922, **44**, 738). The use of copper oxide at 280°C. for the same purpose has also been proposed (King and Edgecombe, D.S.I.R. Fuel Research Tech. Paper No. 33, 1931).

The best method for the determination of small quantities of carbon monoxide is by measuring the amount of iodine liberated when iodine pentoxide is reduced according to the equation :

$$I_2O_5+5CO=5CO_2+I_2$$

Unsaturated hydrocarbons must first be removed and, if the carbon monoxide is to be determined in the gases resulting from a combustion, oxides of nitrogen must also be removed. The gases are passed through caustic potash, calcium chloride, and phosphorus pentoxide, then through iodine pentoxide at 160°C., the iodine liberated being dissolved in potassium iodide solution and the carbon dioxide absorbed by caustic potash solution and soda lime ; both the iodine and carbon dioxide liberated can be determined. Methane is not affected by iodine pentoxide under these conditions. The iodine pentoxide must be pure, the commercial product is best purified by heating to about 210°C. for about 2 days while air or nitrogen is blown through it, to remove any unstable compounds which may be present. The method is claimed to be accurate to 0·002% (*see* Wood and Howarth, Gas. J. 1926, **175**, 787 ; *ibid.* 1927, **178**, 824 ; Davies and Hartley, J.S.C.I. 1927, **46**, 201, T ; Gas. J. 1928, **182**, 880 ; Vandaveer and Gregg, *ibid.* 1929, **187**, 553 ; Edell, Ind. Eng. Chem. 1928, **20**, 275).

Automatic recorders have been used in which the carbon monoxide is burnt over a catalyst, and either the temperature rise measured by a thermocouple, the method being claimed to be sensitive to 1–2 parts carbon monoxide per million (Fieldner, Katz, and Meiter, Eng. News Rec. 1925, **95**, 423) or by mixing the gas with oxygen obtained by the electrolysis of caustic soda solution, and passing the mixture over a catalyst of iron and chromium oxides containing a little ceria and thoria heated to 230°C. The carbon dioxide evolved is absorbed by a solution of calcium hydroxide and the change in conductivity measured (Rideal and Taylor, Analyst, 1919, **44**, 89).

S. W. S.

CARBON SUBOXIDE, C_3O_2. Malonic anhydride.

First isolated by Diels and Wolf, who heated

diethyl malonate with a large excess of phosphorus pentoxide at 300°, the following reaction occurring :

$$CH_2(COOC_2H_5)_2 \rightarrow 2H_2O+2C_2H_4+C_3O_2$$

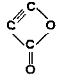
(Ber. 1906, 39, 689). Other esters of malonic acid and malonic acid itself also yield the suboxide when similarly treated (Diels and Meyerheim, Ber. 1907, 40, 355). The poor yields obtained by this method were shown to be due to polymerisation of the carbon suboxide, and Stock and Stoltzenberg (Ber. 1917, 50, 498) by the rapid removal of the reaction products from the phosphorus pentoxide have improved the yield to 25%. Staudinger and Klever (Ber. 1908, 41, 906) claim an 80% yield by the action of zinc upon dibromomalonyl bromide in ether solution, whereas malonyl chloride on treatment with silver oxide gives only 5–10% (Staudinger and Bereza, Ber. 1908, 41, 4461). The most convenient and satisfactory method of preparation, the pyrolysis of diacetyltartaric anhydride, was discovered by Ott (Ber. 1914, 47, 2388) who in this way obtained a yield of 42·5% (Amer. Chem. Abstr. 1923, 17, 36). A yield of 41% using larger quantities of material was made possible by Ott and Schmidt (Ber 1922, 55, [B], 2126), who designed an apparatus in which the vapours of diacetyltartaric anhydride were passed over a heated platinum filament. An improved apparatus raises the yield to 60–73% (Kobe and Reyerson, J Physical Chem. 1931, 35, 3025), while as much as 49% may be obtained by passage of the anhydride vapour through a Pyrex glass tube heated to 625°–650°. Carbon monoxide is said to yield some carbon suboxide on passage through an ozoniser (Ott, Ber. 1925, 58, [B], 772).

Carbon suboxide is a gas with an intolerable odour : in small amount it acts as a lachrymatory and in higher concentration produces a feeling of suffocation. It may be condensed to a mobile liquid, b p. +7°, m.p. −107° to −108° (Diels and Wolf) or −113° (Stock and Stoltzenberg), and of density 1·11 at 0°. The vapour pressure of the liquid has been measured by Stock and Stoltzenberg (l c.), and by Edwards and Williams (J.C.S. 1927, 855) It is quite stable at room temperatures when kept in clean vessels free from all moisture, but the presence of mercury or water vapour effects polymerisation of the gas to a red solid. Liquid carbon suboxide changes within 24 hours to a solid amorphous dark red solid which is soluble in water. The polymerisation of the gas is probably a catalytic surface reaction as its velocity cannot be expressed by any simple formula (Edwards and Williams, l c.). Stock and Stoltzenberg consider the polymerisation to be autocatalytic. The solid red polymer loses carbon dioxide at 37° and is then only partly soluble in water. On further heating carbon dioxide, monoxide, and some suboxide are evolved. After a thorough investigation of the polymerisation of the gas Klemenc, Wechsberg, and Wagner (Z. physikal Chem. 1934, 170, 97, and Z. Electrochem. 1934, 40, 488) conclude that it is an irreversible reaction, catalysed by the walls of the vessel, and follows a unimolecular law after a period of induction. Both gaseous and polymerised material yield carbon dioxide and monoxide at 200°C.; prior to polymerisation at this temperature a carmine red gas is formed, which from absorption spectra data is postulated as C_2, the decomposition of the suboxide being represented by the equation:—

$$C_3O_2 \rightleftharpoons CO_2+C_2$$

Structural formulæ for polymerised carbon suboxide have been suggested by Hartley (Chem. News, 1906, 94, 40) and by Diels, Beckmann, and Tonnies (Annalen, 1924, 439, 76).

The constitution of carbon suboxide has given rise to controversy, but the diketene formula of Diels and Wolf, O=C=C=C=O, is the one usually accepted, although a cyclic formula



suggested by Michael (Ber. 1906, 39, 1915) is possible. The inter atomic distances have been determined by the electron diffraction method (Brockway and Pauling, Proc. Nat Acad. Sci. 1933, 19, 860 ; cf. Boersch, Naturwiss, 1934, 22, 172 ; and Monatsh. 1935, 65, 311)

Chemical properties are similar to those of a diketene; it reacts with water to give malonic acid, with ammonia and amines to give malonamide and malondiamides (Diels and Wolf, l c., and Pauw, Rec trav. chim. 1936, 55, 216), with dry hydrogen chloride to give malonyl chloride, and with bromine to give dibromomalonyl bromide. With formic and acetic acids compounds are given with the properties of mixed anhydrides of malonic acid and formic or acetic acids (Diels and Lahn, Ber. 1908, 41, 3426, Diels, Bechmann, and Tonnies, l.c.). Hydroxylamine yields malonhydroxamic acid (Hurd and Pilgrim, J. Amer. Chem. Soc. 1933, 55, 757), but phenylhydrazine ultimately yields 1-phenyl-3 5-diketopyrazolidine and not the expected malonyl bis-phenylhydrazide (van Alphen, Rec. trav. chim. 1924, 43, 823). With urea a small quantity of barbituric acid is formed, and with o, p, and m-phenylene diamines high-melting, insoluble colourless compounds are produced The reaction of carbon suboxide with sulphur dioxide has been described by Diels and Hansen (Ber. 1926, 59, [B], 2555), and with hydrogen sulphide by Diels, Beckmann, and Tonnies (l c.). Catalytic hydrogenation over nickel or palladium coated silica gel gives carbon dioxide and propylene, and some acetic acid (Kobe and Reyerson, J. physikal. Chem. 1931, 35, 3025).

Carbon suboxide may be quantitatively determined by solution in water and subsequent titration of the malonic acid. Analysis of mixtures of carbon suboxide, monoxide, and dioxide is described by Klemenc, Wechsberg, and Wagner (Monatsh. 1935, 65, 405), accurate assay being possible with as little as 1 c.c. of gas.

Reviews upon the chemistry of carbon suboxide occur in Chemical Reviews, 1930, 7, 479, by Reyerson and Kobe, and in the Journal of Chemical Education, 1931, 8, 232, by Kobe.

CARBON TETRACHLORIDE, TETRACHLORMETHANE, CCl_4. Introduction.—Carbon tetrachloride was discovered by Regnault (Annalen, 1840, 33 332), who prepared it by the action of chlorine on chloroform in sunlight, this preparation being followed by that of Dumas (*ibid.* 1840, 33, 187) by chlorination of methane ; and of Kolbe (*ibid.* 1843, 45, 41 ; 1845, 54, 146) by passing carbon disulphide saturated with chlorine through a red hot tube.

A modification of Kolbe's method is in use to-day for the large scale manufacture of carbon tetrachloride in which chlorination of carbon disulphide takes place at low temperature in the presence of a catalyst, while, so far as is known, the only other technical process which has made any headway on a large scale is that of Dumas. In districts where plentiful supplies of natural gas are available a large amount of research has been carried out on the production of chlorinated hydrocarbons, especially of the methane series by direct chlorination. Difficulties, however, arise in connection with the control of reaction conditions to give one chlorinated product only, and not a mixture of several compounds of differing chlorine content which have to be separated by distillation ; while the large quantities of hydrogen chloride evolved during reaction are not required industrially owing to the extent of the supply from other sources. For these reasons it is very doubtful whether the direct chlorination of methane is used to any large extent on the industrial scale outside the particular areas where natural gas occurs.

Methods of Preparation.—A summary of the extensive literature dealing with the development of the manufacture of carbon tetrachloride is given below.

(*a*) *Chlorination of Carbon Disulphide.*—Early work was concerned largely with examining a variety of catalysts for the Kolbe reaction, described previously, in an attempt to reduce the necessary temperature to a minimum. Hofmann (*ibid.* 1860, 115, 264) showed that antimony pentachloride reacted with carbon disulphide alone, without the addition of chlorine, the mixture warming up, while on cooling, crystals of antimony trichloride mixed with sulphur were deposited, and carbon tetrachloride remained in solution in unconverted carbon disulphide.

Crump (Chem. News, 1886, 14, 154) showed that bromine, and Morel (Compt. rend. 1877, 84, 1460) that iodine, could be used as chlorine carriers, while Serra (Chem. Zentr. 1899, ii, 1098) used iodine in the presence of metallic iron.

A large number of catalysts are available for the reaction, *e.g.* molybdenum pentachloride (Aronheim, Ber. 1876, 9, 1788), the chlorides of phosphorus, arsenic, antimony, and metals of the iron group. Ochi (J. Chem. Ind. Japan, 1919, 22, 897 ; Jap. P. 34917, 1919) investigated the chlorination of carbon disulphide, and showed that antimony pentachloride or iron chloride is the best catalyst, that the yield of carbon tetrachloride is a maximum at 30°C., using 45% excess chlorine (92% CCl_4, 0·5% unchanged CS_2), and that yields decreased at lower temperatures. He recommended that the reaction should be carried out in two stages and in connection with the corrosion problem, stated that nickel was the best constructional material, followed in order by lead, copper, iron and tin. Purification of the tetrachloride was by distillation.

The actual manufacture of carbon tetrachloride takes place essentially in two stages, the first being the formation of the tetrachloride and sulphur chloride in the presence of a catalyst ; followed by interaction of the sulphur chloride formed with a fresh supply of carbon disulphide in contact with iron filings, giving rise to more carbon tetrachloride and sulphur. The latter is separated from the reaction product by crystallisation and is used again in the manufacture of carbon disulphide (Urbain, J.S.C.I. 1902, 20, 926 ; B.P. 13733 ; The Isco Chem. Co. U.S.P. 1260621, 1260622). The reactions can be represented as follows :

$$CS_2+3Cl_2=CCl_4+S_2Cl_2$$
$$CS_2+2S_2Cl_2=CCl_4+6S$$

Howarth and Baker (J.S.C.I. 1906, 25, 559) attempt to reduce the amount of sulphur separated during the second stage of the reaction by chlorinating the sulphur monochloride obtained in the first stage to sulphur dichloride before adding the second quantity of carbon disulphide :

$$CS_2+2SCl_2=CCl_4+4S$$

The presence of a number of intermediate carbon chlorosulphides has been shown by carrying out the chlorination with restricted quantities of chlorine (Klason, Ber. 1887, 20, 2376 ; Delepine and Giron, Bull. Soc. chim. 1923, 32 1785).

The large-scale production of carbon tetrachloride is carried out in lead or lead-lined vessels which can be cooled so that the temperature does not exceed 30°C. A considerable increase in volume takes place during the reaction, the end-point of which is reached when the mixture turns red. The mixture is then fractionally distilled to remove carbon tetrachloride from the sulphur chloride, and the latter is transferred to a second lead vessel provided with a stirrer and more carbon disulphide added with agitation. This mixture is warmed to about 60°C. to complete the reaction, is then cooled to allow the sulphur to crystallise, and finally distilled to remove the carbon tetrachloride which is added to that previously obtained, and purified by distillation from lead vessels, dried, and finally distilled from iron vessels using a fractionating column.

Brallier, Dunlop, and Muggleton (Niagara Smelting Corp. U.S.P. 1817123, 1931) describe apparatus for the chlorination of carbon disulphide.

A bibliography of work on the manufacture of carbon tetrachloride from carbon disulphide together with corrosion data is given in U.S.S.R. Soc. Inst. Research. Sup. Council Dat. Econ. State Inst. App. Chem. 1932, 15, 8–39.

(*b*) *Chlorination of Methane.*—An early reference to the chlorination of methane is that of Walter (G.P. 222919, 1908), who led a mixture of 1 vol. of methane and 4 vols. of chlorine through a glass tube, irradiated with U.V.

light from a quartz mercury vapour lamp. 45% conversion of methane to carbon tetrachloride *with quantities of methyl and methylene* chlorides, and chloroform was obtained.

Tolloczko and Kling (Abhandl. d. Krakauer Akad. d. Wissensch. 1912, 52, 295, 316; Chem. Zentr. 1913, 11, 98) chlorinated natural gas at *400°C., with excess chlorine in the presence of* a catalyst, and obtained 78% carbon tetrachloride in the main fraction boiling below 150°C., while hexachloroethane and other higher compounds were also formed. With excess of hydrocarbons, the main products were methyl and methylene chlorides, with traces of chloroform and carbon tetrachloride. Chlorination in U.V. light at 80°–100° confirmed the above results, using excess and deficiency of chlorine respectively.

Baskerville and Riederer (Ind. Eng. Chem. 1913, 5, 5) chlorinated natural gas containing from 50–90% of methane in the silent electric discharge, or in U.V. light. A mixture of chloroform, carbon tetrachloride, and hexachloroethane was obtained with the tetrachloride as chief product. Bedford (*ibid.* 1916, 8, 1090) showed that with deficiency of chlorine the yield of carbon tetrachloride was only 4–5%.

Jones and Allison (*ibid.* 1919, 11, 639), and Jones, Allison, and Meighan (Bur. Mines Tech. Paper, 1921, No. 255, p. 44) examined the chlorination in detail, and showed that the *reaction begins in the dark at 250°, but that* temperatures between 300°–400°C. are best. The heat of reaction was determined at 400°C., as 137,000 g.-cal.

Pfeifer and Mauthner (B.P. 157253, 1921) by *reaction between chlorine and hydrocarbons at* 150°–50°C. in contact with metals or metallic salts, *e.g.* Fe, Cu, Sb, obtain a wide series of derivatives from methane. Tizard, Chapman, and Taylor (B.P. 214293, 1922) pass methane over pumice impregnated with copper chloride at 435°C., and obtain a similar series with carbon tetrachloride and chloroform as main products. The copper chloride is reduced to cuprous chloride during the reaction, but is regenerated by chlorine.

Carter and Coxe (B.P. 245911; U.S.P. 1572513, 1926; G.P. 472421; F.P. 597678) pass a mixture of methane, methyl chloride, and chlorine through a tube at 400°–500°C., and obtain 80% of methylene chloride with smaller quantities of the other compounds. The reaction was investigated by Boswell and McLoughlin (Canad. J. Res. 1929, 1, 240) in two stages, (*a*) the formation of methyl chloride, using 10 vols. nitrogen to 1 vol. methane as diluent; and (*b*) the formation of carbon tetrachloride without nitrogen as diluent. It was shown that with only a small excess of *chlorine over theoretical and in the absence of* nitrogen at 450°C., carbon tetrachloride was formed in 90% yield. Can. P. 301542, 1930, covers the work described in this paper.

Bodenstein, Günther, and Hoffmeister (Z. *angew. Chem. 1926, 39, 875) measured the heats* of reaction:

(*a*) $C+2Cl_2=CCl_4+25{,}430(\pm 350)$ g.-cal.

(*b*) $CCl_4+2H_2=C+4HCl+62{,}570(\pm 350)$ g.-cal.;

and showed that the equilibrium constant was 0.2 at 600°K. (*cf. also* Bodenstein and others, *Trans. Electrochem. Soc.* 1926, 25, 49; Z. angew. Chem. 1930, 43, 423).

B.P. 486952 of the I.G. Farbenind. A.-G. (Ernst and Wahl) passes a mixture of methane, oxygen, and hydrogen chloride over a catalyst *at 300°–450°C. Chlorine is produced by* the Deacon reaction, and forms chlorinated hydrocarbons. For example, 2 parts methane, 1 part oxygen, and 2 parts hydrogen chloride are passed over pumice impregnated with copper chloride at 400°C.

Holzverkohlungs-Industrie A.-G. (G.P. 477494, 478083) chlorinate methane at 400°C. or over, with or without catalysts, and I.C.I. Ltd. (B.P. 342329, 1929) cover the chlorination of hydrocarbons of low carbon content in packed or unpacked tubes at temperatures above 650° (*e.g.* 800°–850°), using high space velocity.

B.P. 341878, 1929, of H. Dreyfus covers the production of highly chlorinated products (*e.g.* CCl_4) from methyl alcohol by chlorination with phosphorus or sulphur chlorides, with or without free halogen, in the presence of a diluent, and under pressure.

(*c*) *Miscellaneous Methods.*—A number of electric heating processes have been suggested. A mixture of sodium chloride and silica is heated in the lowest portion of a furnace lined with magnesia, and provided with three sets of *electrodes, one above the other. The middle* electrodes heat a mass of coke, and the chlorine from the alkali chloride reacts with the incandescent carbon, forming carbon tetrachloride which, after passing through the arcs between *the third set of electrodes, is distilled off. The* temperature does not exceed 2,000° (Machalske and Lyon, J.S.C.I. 1903, 22, 1298; Machalske Chem. Zentr. 1904, 1, 1069). The chlorine can also be supplied from an external source, the carbon only being electrically heated (Maywald, J.S.C.I. 1907, 26, 1253).

Another process consists in heating together lime, calcium chloride, and carbon in the absence of air in an electric furnace, in the proportions indicated by the equation:

$$2CaO+2CaCl_2+10C=4CaC_2+2COCl_2$$

The carbonyl chloride is led over heated coke, animal charcoal or pumice, where it is decomposed into carbon tetrachloride and carbon dioxide by surface contact (Machalske and Darlington, J.S.C.I. 1906, 25, 559).

A mixture of calcium chloride and coke *heated in the electric furnace in* a stream of chlorine also yields carbon tetrachloride (Matthews and Darlington, *ibid.* 1906, 25, 1232).

The halogenation of metallic or other carbides, *such as acetylene, also yields carbon halides,* so long as the temperature is kept below the dissociation point of the halide required (Blackmore, *ibid.* 1908, 27, 712).

PURIFICATION.—Carbon tetrachloride as obtained from carbon disulphide is *purified by* chemical means, dried, and then distilled. Suitable purification methods are those of Schmitz-Dumont (Chem.-Ztg. 1897, 21, 511), viz. caustic soda and alcohol; and Van Ardsel

and Vannah (U.S.P. 1697483, 1925), viz. alkaline sulphide solutions.

Drying is normally carried out in a tower system with concentrated vitriol, although according to Neuville and Mange (F.P. 649934, 1928) anhydrous calcium, zinc or barium chlorides, sodium sulphate or carbonate, alum, ammonium and magnesium carbonates may be used.

The final distillation of the dry product takes place in an iron still with reflux (*cf.* Chem. Fabrik auf Aktien, G.P. 432849, 1926). The product obtained as vapour mixed with small quantities of methyl and methylene chlorides and chloroform from the chlorination of methane can be condensed and purified by fractional distillation, or can be recovered from the exit gases by adsorption on charcoal or silica gel, advantage being taken of the differential rates of adsorption of the various chlorinated compounds to effect a preliminary separation, and afterward dried and distilled in the usual manner. Patents covering recovery by charcoal or silica gel are those of Burrell, Voress and Canter (U.S.P. 1382390, 1921); Silica Gel Corporation (B.P. 195055, 1923); I.G. Farbenind. A.-G. (B.P. 296301, 1928).

The product comes on the market containing only a trace of moisture, free from sulphur and sulphur compounds, and is sold in carboys, in 50-gallon drums, and in tank wagons.

PROPERTIES.—(*a*) *Physical.*—Carbon tetrachloride is a transparent, colourless liquid with a pungent odour.

B.p. 76·74°C. (Thorpe, J.C.S. 1880, **37**, 201); m.p. −22·7°C.

Density, d_4^0 1·6326, d_4^{15} 1·6057, d_4^{20} 1·5944; vapour density at N.T.P. 5·30 (air=1); vapour pressure (mm. Hg) 33/0°C., 91/20°, 215/40°, 447/60°, 621/70°, 723/75° (Schreinemakers, Z. physikal. Chem. 1904, **48**, 445); latent heat of vaporisation (cals. per g.) 52·0/0°C., 46·35/76·2°, 46·0/80°, 44·15/100° (Mathews, J. Amer. Chem. Soc. 1926, **48**, 562).

Specific heat of liquid increases regularly from 0·2010/0° to 0·2031/70°, specific heat of vapour 0·14/0°, 0·115/70° (Mills and MacRae, J. Physical Chem. 1911, **15**, 54; *cf. also* Williams and Daniels, J. Amer. Chem. Soc. 1924, **46**, 903, 1569). Specific heat=0·1852–0·00047*t* (°C.) (Timmermans and Martin, J. Chim. phys. 1926, **23**, 747).

Solid carbon tetrachloride is trimorphous (Tammann, Annalen, 1898, **301**, 489) the three modifications melting at −28·6°, −23·73°, and −21·2° respectively, the second being the form usually obtained. Refractive index (D line) is 1·4658.

Solubility in water (g. per 100 g.): 0·097/0°, 0·083/10°, 0·080/20°, 0·085/30° (Rex, Z. physikal. Chem. 1906, **55**, 355); 0·077/15°, 0·081/30° (Gross and Saylor, J. Amer. Chem. Soc. 1931, **53**, 1744).

Solubility in carbon tetrachloride of (*a*) water (g. per 100 g.): 0·00711/10°, 0·00844/20°, 0·0109/30°, 0·0152/40°, 0·0237/50° (Rosenbaum and Walton, J. Amer. Chem. Soc. 1930, **52**, 3568); of (*b*) sulphur (g. per 100 g.): 0·645/15·5°, 0·723/18°, 0·754/22° (Delaplace, J. Pharm. Chim. 1922, **26**, 139); of (*c*) chlorine, solubility coefficient=0·031±0·003/19° (Schwab and Hanke, Z. physikal. Chem. 1924, **114**, 251).

The adsorption of carbon tetrachloride on charcoal and silica and alumina gels has received attention from a large number of workers: Berl and Andress (Z. angew. Chem. 1921, **34**, 369) give data for adsorption of tetrachloride on charcoal activated by zinc chloride; Coolidge (J. Amer. Chem. Soc. 1924, **46**, 569) examined the adsorption on carefully purified charcoal; Perry (J. Physical Chem. 1925, **29**, 1462) showed that 10 g. of alumina gel adsorbed 3·6 g. carbon tetrachloride at 25°C.; Patrick, Frazer and Rush (*ibid.* 1927, **31**, 1511) used carbon tetrachloride in a study of the properties of silica gel at various temperatures; Pearce and McKinley (*ibid.* 1928, **32**, 360) determined the heat of adsorption on coconut charcoal at 25°C.; Pearce and Johnstone (*ibid.* 1930, **34**, 1260), and Pearce and Reed (*ibid.* 1931, **35**, 905) determined the adsorption on charcoal of the gases formed by the chlorination of methane.

(*b*) *Chemical.*—Dry carbon tetrachloride is a stable compound, and can be heated in contact with dry metals to fairly high temperatures without decomposition. In the presence of moisture, however, it rapidly hydrolyses when heated, liberating phosgene and hydrogen chloride,

$$CCl_4+H_2O=COCl_2+2HCl,$$

a reaction which is of considerable technical importance, for it causes great difficulties in the choice of materials for handling hot moist carbon tetrachloride, and also makes the use of tetrachloride fire extinguishers in closed rooms and buildings a dangerous procedure owing to the intensely poisonous nature of carbonyl chloride. Doughty (J. Amer. Chem. Soc. 1917, **39**, 2685) showed that the hydrolysis of pure carbon tetrachloride by pure water at ordinary temperatures was negligible, but was accelerated by the presence of iron and copper, and became very marked at elevated temperatures.

The corrosion of various metals by dry and moist carbon tetrachloride has been examined by Bolis (Chem.-Ztg. 1907, **30**, 1117); Rhodes and Carty (Ind. Eng. Chem. 1925, **17**, 909), who showed that nickel is the metal most resistant to cold carbon tetrachloride (wet and dry), and tin to the damp vapour. Aluminium reacted with dry tetrachloride to form aluminium chloride and hexachloroethane. Formánek (Chem. Zentr. 1930, **11**, 976) states that the corrosion in the cold of copper, brass, tin and iron by tetrachloroethane and trichloroethylene is more in 8 weeks than by that of carbon tetrachloride in 8 months.

Reduction of carbon tetrachloride by hydrogen in the presence of pumice yields methane and ethylene (Berthelot, Ann. Chim. Phys. 1858, [iii], **53**, 69); using reduced nickel as catalyst, hexachloroethane is formed at 270°, while with excess of hydrogen and nickel, tetrachloroethane is produced (Sabatier and Mailhe, Compt. rend. 1904, **138**, 407).

Ferrous hydroxide and a base or basic salt causes substitution of chlorine by hydrogen

(Soc. des Usines Chim. Rhône Poulenc, B.P. 225174, 1923; Can. P. 250594, 1925), complete substitution of chlorine by bromine occurs readily by heating with aluminium bromide (Gustavson, Bull Soc. chim. 1881, [ii], 35, 556); and by treating carbon tetrachloride at the boiling-point with fluorine a mixture of CCl_3F, CCl_2F_2, and CF_4 is formed (Ruff and Keim, Z. anorg. Chem. 1931, 201, 245).

The action of sulphur gives rise to a number of carbon sulphochlorides, the final product being carbon disulphide (Klason, Ber. 1887, 20, 2376); *cf. method of manufacture.*

Chlorsulphonic acid and phosgene are formed by the action of fuming sulphuric acid (45% SO_3) on carbon tetrachloride (Lepin, J. Russ. Phys. Chem. Soc. 1920, 52, 1).

USES.—The principal uses of carbon tetrachloride are as solvent, dry cleaning agent, fire extinguisher, and insecticide.

(*a*) *Solvent.*—The product possesses high solvent power for a large variety of organic and inorganic compounds, and finds use in the preparation of floor polishes, shoe-cleaning materials, as solvent for various lacquers, asphalts, resins, etc, and in considerable quantities in the rubber industry for adhesive solutions, and in the cold vulcanisation process.

Owing to its non inflammability it has displaced acetone and benzene very largely in the lacquer industry.

The general adoption of carbon tetrachloride as solvent is slower than would be expected from its desirable properties, but owing to its narcotic action, coupled with the fact that trichlorethylene, which is an equally good solvent, and also non inflammable, is available commercially, a large number of users prefer the latter. For literature on carbon tetrachloride poisoning, *see* Lewis (Z. deut. Oel Fett. Ind 1920, 40, 421, 439); "Lehrbuch der Toxicologie," 1929, Ferzer and others (Ind. Eng. Chem. 1922, 14, 456); Davis (Rubber Age, 1929, 25, 367); Lehmann (Zentr. Gewerb-hygiene, 1930, 7, Part 5, 123). A comprehensive article on the toxicity of carbon tetrachloride containing a bibliography of over 100 references is to be found in Report No 80 of the Medical Research Council Industrial Health Research Board, "Toxicity of Industrial Organic Solvents," 1937, pp. 136–161, published by H M. Stationery Office.

It has been stated that the narcotic action of carbon tetrachloride is about 50% greater than that of chloroform and about equal to that of benzene.

(*b*) *Dry Cleaning.*—The large number of fires caused by benzine used for the dry cleaning of goods has restricted its use to conditions under which special precautions are necessary. Non-inflammable solvents such as carbon tetrachloride and trichloroethylene are therefore active competitors to benzine as dry-cleaning agents, in which respect there seems little to choose between them (see Vol. I, 130b)

(*c*) *Fire Extinguishers.*—Considerable attention has been paid to the uses of carbon tetrachloride as fire extinguisher, chiefly on account of its reputed danger owing to decomposition to phosgene when heated in presence of moisture. The net result of the investigations, some of which are listed below, is that carbon tetrachloride extinguishers are definitely dangerous when used in confined spaces owing to phosgene formation, but in the open air this risk is very slight.

See the following: Fieldner, Katz, Kinney and Longfellow (J. Franklin Inst. 1920, 190, 543); Fieldner, Katz and Kinney (Bur. Mines Tech. Paper, 1921, No. 248, p. 66); Fohlen (Tech. Moderne, 1922, 14, 593); Voigt (Chem.-Ztg. 1925, 49, 937); Dufraisse and Horclois (Compt. rend. 1931, 192, 564); Alice Hamilton (Ind. Eng. Chem. 1933, 25, 539).

The I.G. Farbenind. A.-G. have patents covering the prevention of phosgene formation from carbon tetrachloride in fire extinguishers consisting of the addition to the tetrachloride of ammonia, a hydrocarbon or organic phosphate, and/or a suitable oil or fat in small quantities (B.P. 317843, 1928, 319320, 331147; G.P. 513191).

(*d*) *Insecticide.*—Carbon tetrachloride possesses insecticidal action, and has recently been used for fumigation of crops (Joachmoglu, Biochem. Z. 1921, 124, 134) and stored goods (Cotton and Roark, J. Econ. Entomol. 1927, 20, 636).

Hoyt (Ind Eng. Chem. 1928, 20, 460) showed that 100% kill of insects infesting flour, clothing, and furniture in a store was obtained with a dosage of 14 lb. of mixture containing 3 parts of ethylene dichloride to 1 of carbon tetrachloride per 1,000 cu ft at 82°F. for 24 hours. The store had to be made gas tight before the test.

Further work by Hoyt (*ibid.* 1928, 20, 835, 931) and Thomas (J. Comm. Sci. Ind. Res. 1929, 2, 128) confirmed previous results.

STATISTICS.—Production statistics in respect of carbon tetrachloride for the chief manufacturing countries are not available as the relevant figures are normally included in returns showing the production of a wide range of solvents. F. R.

CARBONADO or "black diamond" (known in the trade as "carbon" or "carbonate") is a finely granular crystalline material, dull, black, and opaque.

"CARBONALPHA" *v.* CARBON, *Carbon Black* or *Gas Black.*

CARBONIC ANHYDRASE is the name given to an enzyme separated from red blood corpuscles by Meldrum and Roughton (J. Physiol. 1933, 80, 113, 143). Unlike many enzymes it catalyses reactions which proceed at an appreciable rate in its absence. Its function is to accelerate the formation of carbon dioxide from bicarbonate in the lung blood vessels of air-breathing animals. It may have other possibilities in earlier stages of metabolism. There is enough in human blood to accelerate the reaction about 2,000 times at 15°C. and 600 times at 37°C. A method of measuring the activity has been devised by the authors. It is obtained by shaking a mixture of 10 c.c. washed ox corpuscles with 6 c.c. H_2O+4 c.c. $EtOH$, to which 5 c.c. of chloroform are added. On centrifuging the enzyme solution is in the top layer of a three-phase system and yields a brown

solid on evaporation in a vacuum desiccator. It can be purified by $Al(OH)_3$ adsorption when it shows no catalase, oxidase or peroxidase reactions. It is then relatively undialysable, is stable to temperatures up to 65°, is destroyed in buffer solutions outside the range p_H 4–11 and gives positive results with the various protein tests. It has been found in the blood of all vertebrates but not in milk, urine or plasma. *It is absent from green plant material and yeast.*

E. F. A.

CARBONITE, or natural coke. A coke-like material formed by the baking action of intrusive igneous rock-masses on seams of bituminous coal. Found in Ayrshire and in Chesterfield Co., Virginia.

L. J. S.

CARBONYLS, METAL. Compounds of the heavy metals with carbon monoxide.

The first compound of this type, nickel carbonyl, $Ni(CO)_4$, was discovered by Mond, Langer and Quincke (J.C.S. 1890, 57, 749). Since that date, carbonyls of iron, cobalt, chromium, molybdenum, tungsten and ruthenium have been prepared. Of these, the nickel, iron, and probably the molybdenum compound have found extensive technical application. Chemically, these compounds form a group of especial interest in that, in contrast to the other compounds of the transition metals, they are volatile and diamagnetic.

The carbonyls of nickel, iron, cobalt and molybdenum are obtained by the action of carbon monoxide upon the reduced metal. For the laboratory preparation of *nickel carbonyl*, nickel is reduced from the oxalate (Laird, Rec. trav. chim. 1927, 46, 177; v. Duin, *ibid.* 381) or from the hydrated oxide at temperatures below 300°. The metal is cooled in hydrogen, and carbon monoxide is admitted in the cold. Rapid adsorption occurs, with much evolution of heat. The carbonyl formed may be disengaged by cautious warming. *Iron carbonyl*, $Fe(CO)_5$, may be prepared similarly, but reaction occurs readily only at high pressures, when specially active iron is not essential. At high pressures reaction occurs even with massive iron, so that carbon monoxide or coal gas stored under pressure is always liable to contain iron pentacarbonyl, which may be formed in considerable quantity in such circumstances (Mittasch, Z. angew. Chem. 1928, 41, 827; Friend, J.C.S. 1930, 718). Traces from a similar source may be present in synthetic methanol. Iron carbonyl is now produced on a technical scale by employment of pressures of 100–200 atm. Small amounts of copper may be added, which accelerate the reaction, and permit of reduction at lower temperatures (B.P. 319356, 1928). *Molybdenum carbonyl*, $Mo(CO)_6$, may be prepared by the action of carbon monoxide on the metal reduced from the oxychloride (Mond, Hirtz and Cowap, J.C.S. 1910, 97, 798) or, technically, reduced from the oxide in presence of copper. According to Mittasch (*l.c.*), by paying attention to the purity of the materials, and especially to that of the carbon monoxide, combination with iron and molybdenum may be made to proceed as avidly as with nickel.

Chromium carbonyl, $Cr(CO)_6$ (Job and Cassal, Compt. rend. 1926, 183, 392), and *tungsten carbonyl*, $W(CO)_6$ (Job and Rouvillois, Compt. rend. 1928, 187, 564), have been prepared by the action of a Grignard reagent on sublimed chromic chloride or tungsten hexachloride respectively, in presence of carbon monoxide. Molybdenum carbonyl may be prepared similarly (Hieber and Romberg, Z. anorg. Chem. 1935, 221, 321).

Ruthenium was at first described (Mond, Hirtz, and Cowap, *l.c.*) as forming a yellow-orange compound with carbon monoxide but at 180° and 200 atm., a small amount of the liquid $Ru(CO)_5$ is formed. The same compound is readily obtained by the action of carbon monoxide on $RuI_2{\cdot}2CO$ in presence of silver at 170° and atmospheric pressure, or at 100° and 250 atm., or—without isolating $RuI_2{\cdot}2CO$—by heating RuI_3 with 5 parts of "molecular" silver in carbon monoxide at 170° and 450 atm. (Manchot and Manchot, Z. anorg. Chem. 1936, 226, 370).

The so-called carbonyls of the alkali metals are of entirely different constitution. The explosive compound formed by heating potassium in carbon monoxide (Nietzki and Benckiser, Ber. 1885, 18, 499, 1833) is $K_6C_6O_6$, a salt of hexahydroxybenzene. The compounds formed with potassium, sodium, lithium, calcium, barium, etc., in liquid ammonia (*see e.g.* Joannis, Compt. rend. 1893, 116, 1518; Roederer, Bull. Soc. chim. 1906, [iii], 35, 715; Pearson, Nature, 1933, 131, 166) are of unknown nature.

The monomeric carbonyls $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, $Ru(CO)_5$, $W(CO)_6$, are volatile, the polynuclear compounds $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $Ru_2(CO)_9$ are non-volatile or slightly volatile solids. They are all decomposed by heating, with deposition of a metal mirror; the stability is greatest in the case of $Cr(CO)_6$, which is appreciably decomposed only above 140°. They are attacked and decomposed by the halogens and by strong oxidising agents. The volatile compounds, especially nickel carbonyl, are extremely toxic (Armit, J. Hygiene, 1907, 7, 525; 9, 249).

Nickel Carbonyl, $Ni(CO)_4$, b.p. 43°, m.p. −22°, *d* 1·325 at 14°, is a colourless, highly refractive liquid. Dissociation of the vapour commences above 40°, and is nearly complete at 180°. Halogens cause immediate decomposition :

$$Ni(CO)_4+Br_2=NiBr_2+4CO$$

Reaction occurs also with phosphorus (Grieb and Jones, J.C.S. 1932, 2543), forming NiP and possibly NiP_4, and with carbon disulphide vapour, forming NiS (Dewar and Jones, J.C.S. 1910, 97, 1226). Oxidising agents, or moist air, also cause decomposition, forming basic carbonates, etc. By the action of pyridine or *o*-phenanthroline, however, only a portion of the carbon monoxide is displaced, forming compounds

$$Ni_2(CO)_4(C_5H_5N)_3 \text{ and } Ni(CO)_2(C_{12}H_8N_2)$$

(Hieber, Mühlbauer, and Ehmann, Ber. 1932, 65, [B], 1090).

The thermal decomposition of nickel carbonyl finds its principal application in the Mond process for separating nickel from the Sudbury copper-nickel matte. The nickel deposited is said to be especially suited for anodes for nickel plating, and is the only source of completely cobalt-free nickel. The nickel coating of mirrors and Dewar flasks by the process has also been proposed (Fink and King, Trans. Amer. Electrochem. Soc. 1928, 54, 397).

Iron Pentacarbonyl, $Fe(CO)_5$, b.p. 102°, m.p. −21°, d 1.4664 at 18° is a yellow liquid. In sunlight it undergoes photochemical decomposition, forming *iron nonacarbonyl*, $Fe_2(CO)_9$ (Dewar and Jones, Proc. Roy. Soc. 1906, 79, 66; Warburg and Negelein, Biochem. Z. 1928, 200, 414). The latter decomposes on heating into iron pentacarbonyl and *iron tetracarbonyl*, $Fe_3(CO)_{12}$, *which may be more conveniently* obtained by the oxidation of *iron carbonyl hydride*, $Fe(CO)_4H_2$.

Alkali salts of iron carbonyl hydride are obtained by the action of alkalis, especially in alcoholic solution, on iron pentacarbonyl (Hieber and Leutert, Z. anorg. Chem. 1932, 204, 145):

$$Fe(CO)_5+4NaOH = Fe(CO)_4Na_2+Na_2CO_3+2H_2O$$

On addition of acid, the carbonyl hydride is liberated as a volatile, very reactive liquid, which may be quantitatively oxidised, without being isolated, to iron tetracarbonyl, *e.g.*

$$3Fe(CO)_4H_2+3H_2O_2=Fe_3(CO)_{12}+6H_2O$$

(Hieber, Z. anorg. Chem. 1932, 204, 165).

Mercury salts react directly with iron pentacarbonyl, forming the corresponding mercury salt (Hock and Stuhlmann, Ber. 1929, 62, [B], 431):

$$Fe(CO)_5+HgSO_4+H_2O = Fe(CO)_4Hg+CO_2+H_2SO_4$$

This reaction may be used for the separation of small amounts of iron pentacarbonyl.

The iron carbonyls undergo numerous reactions in which the carbon monoxide is only partially displaced from the molecule. Thus the halogens form unstable addition compounds $Fe(CO)_5X_2$, which break down at the ordinary temperature to compounds $Fe(CO)_4X_2$. These, in the light, or with water, yield the pure iron halides and carbon monoxide (Hieber and Bader, Ber. 1928, 61, [B], 1717). CO in the carbonyls and the carbonyl halides is replaceable by pyridine, ethylenediamine and other compounds, forming compounds with a lower ratio CO:Fe, such as

$$Fe_2(CO)_4(C_5H_5N)_3,\ Fe(CO)_2(C_5H_5N)$$

etc. This replaceability of CO by amines is characteristic of the carbonyls and shows that the CO, like the amines, is co-ordinatively attached to the metal atom.

Iron tetracarbonyl undergoes reactions similar to those of $Fe(CO)_5$, but is more reactive. With nitric oxide it forms the compound $Fe(CO)_2(NO)_2$, which reacts similarly to the carbonyls proper, and forms derivatives containing no CO, *e.g.* $Fe(NO)_2(C_{12}H_8N_2)$ (J. S. Anderson, Z. anorg. Chem. 1932, 208, 238).

Ruthenium pentacarbonyl, $Ru(CO)_5$, m.p. −22°, closely resembles the iron compound in its reactions. Thus it forms $Ru_2(CO)_9$ by photo-decomposition, and probably $Ru_3(CO)_{12}$ at higher temperatures.

Cobalt tetracarbonyl, $Co_2(CO)_8$, is an orange, slightly volatile solid, which decomposes above its m.p. (52°) to form $Co_4(CO)_{12}$. Its chemical behaviour is similar to that of iron carbonyl. With nitric oxide it forms a volatile nitrosocarbonyl, $Co(CO)_3NO$, and gives rise also to the unstable volatile hydride, $Co(CO)_4H$.

Chromium, molybdenum and tungsten carbonyls are colourless crystalline bodies, subliming without fusion. They are characterised by great stability, being inert to the action of *bromine, but attacked by aqua regia. Chromium* and tungsten carbonyls have not, as yet, found technical application.

The decomposition of the metal carbonyls on hot surfaces gives rise, as already stated, to compact mirror deposits. Owing to catalytic decomposition of the carbon monoxide, $2CO \rightarrow C+CO_2$, the metal so deposited contains free carbon and, in the case of iron carbonyl, Fe_3C. By decomposition in the gas phase, however, a finely divided product is obtained, containing some free carbon and a little oxide. By re-fusing this in an induction furnace with the theoretical quantity of pure ferric oxide (also obtained by oxidation of iron carbonyl), an extremely pure metal may be obtained, containing less than 0.0007% of carbon and 0.01% of oxygen (Mittasch, Z. angew. Chem. 1928, 41, 827; F.P. 690981, 1929). This so called *carbonyl iron* finds application for the preparation of catalysts and for magnet and transformer cores.

The metal carbonyls have been used as antiknock agents (C. K. Reiman, Ind. Eng. Chem. 1927, 19, 1055; Olin and Jebens, *ibid.* 1929, 21, 43; Sims and Mardles, Engineering, 1926, 121, 774), as have the addition compounds of iron and molybdenum carbonyls with ethylamine, etc. (U.S.P. 1780643, 1927). The use of *carbonyls as catalysts in the polymerisation of* fatty esters has also been proposed (B.P. 340004).

Metal carbonyls in the air may be detected and estimated by passing through nitric acid and over I_2O_5 to oxidise the carbon monoxide (Lucas and Grassner, Mikrochem., Emich Festschrift, 1930, 197). According to Clark, Hardy, and Wilman, $5–6\times10^{-7}$ g. of Fe (as carbonyl) per c.c. of air may be detected by its effect on the ultra-violet spectrum of a petrol flame.

A bibliography of the scientific, technical, and patent literature of the carbonyls to 1930 is given by Mond (J.S.C.I. Trans. 1930, 49, 288).

J. S. A.

CARBORAFFIN. Activated carbon, prepared by mixing the raw material (sawdust, peat, etc.) with zinc chloride, carbonising at 550°, washing to remove zinc chloride, drying, and grinding. Used in sugar refining.

CARBORUNDUM, SiC. Crystalline silicon carbide.

About 1890 E. G. Acheson, *in attempting to*

crystallise carbon, by dissolving it in aluminium silicate, in an electric arc, obtained some blue crystals which he assumed must be a compound of carbon and alumina (corundum) and suggested the name "carborundum." Analysis, however, proved that they were in fact silicon carbide, a compound which had been studied by Schützenberger, Colson, Moissan, and others (for fuller details, *see* Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, p. 875). The commercial production was begun about 1892, by the Carborundum Co., at Niagara Falls, U.S.A., and also in Canada, under Acheson's patent (*cf.* B.P. 17911, 1892).

Preparation.—Amorphous silicon carbide is formed as a greenish powder by heating carbon and silica together at about 1,200°C. (Schützenberger, Compt. rend. 1892, **114**, 1089), but carborundum is only formed at a temperature of 1950°C. (Tucker and Lampen, J. Amer. Chem. Soc. 1906, **28**, 853). Their experiments were made with an industrial furnace and they found the temperature of decomposition of carborundum into graphite and silicon to be 2,220°C. Gillett, working with an experimental furnace, confirmed that figure, but gave the temperature of formation as 1,540°C. (J. Physical Chem. 1911, **15**, 213). By means of the electric arc, Moissan obtained pure silicon carbide, in the form of pale green crystals, from the vapours of carbon and silicon (Compt. rend. 1893, **117**, 423).

The method of manufacture used at Niagara, remains substantially the same, and is as follows: The furnaces are built of firebrick and are about 16 ft. long, 5 ft. high and 5 ft. wide. The ends are solid, about 2 ft. thick, and carry the terminals. Each terminal consists of 60 carbon rods, 30 in. long and 3 in. diameter, into the ends of which fit copper plugs, which in turn fit into sockets in a square copper plate bolted to the outside of the wall, and connected with the leads. Only the end walls and the bed are permanent; the sides are built up with the charge and are taken down to remove the product.

In charging, the furnace is half filled with the materials, which must not touch the electrodes; and a cylindrical core 21 in. diameter, composed of pieces of coke $\frac{1}{2}$–$\frac{3}{4}$-in. diameter, is built up between the electrodes. Over this the charge is built up to a height of 8 ft. The current passes through the coke and forms numerous arcs which heat the charge to a very high temperature. The charge is composed of:

Coke	34·2 parts.
Sand	54·2 ,,
Sawdust	9·9 ,,
Common salt	1·7 ,,

The salt is added as a flux; the sawdust to increase the porosity of the charge and thus allow the escape of the carbon monoxide formed in the reaction:

$$SiO_2+2C=Si+2CO$$
$$Si+C=SiC$$

During the run, about 6 tons of this gas are given off and are allowed to burn at the top of the furnace.

The alternating current supplied by the Niagara Power Co. at 2,200 volts is transformed down to 165 volts, and a large water rheostat is used to regulate or interrupt the current, the usual means being too dangerous with the heavy currents used. At the beginning of a run the E.M.F. is 165 volts, but within $1\frac{1}{2}$ hours the resistance falls and the E.M.F. is reduced to 125 volts; during this period, the current increases from 1,700 to 6,000 amps. The conditions then remain steady during the whole run of 36 hours.

The charge per furnace is about 30,000 lb., of which the core forms about 3%, the energy used is about 26,400 kilowatt-hours, and the product consists of about 6,700 lb. of carborundum and 5,000 lb. of amorphous silicon carbide. In other words, about 4 kilowatt-hours are required for the production of 1 lb. of carborundum.

A modification of the process consists in preheating the charge by combustion of gaseous or solid fuel (Tone and the Carborundum Co., U.S.P. 908357, 1908). By moving the arc zone from the material formed, in the direction of the unreduced mixture, a column of silicon is built up under the electrodes, and by removing portions of the carbide and supplying fresh material, the process can be made continuous (*idem.* U.S.P. 937119, 1909).

The carborundum is dug out in large masses and pounded with water in a mechanical crusher, and then digested with sulphuric acid (1:2) for 3 days at 100°C. and finally washed with water. The finer portions which are washed away are collected separately and known as "flours." The residue is dried in a kiln and graded through a system of screens. The finest powders are graded by the time they remain in suspension in water and are designated as 1-, 3-, 4-minute powders (Kohn, J.S.C.I. 1897, **16**, 863).

The following table gives the composition of some of these products:

	I.	II.	III.	IV.	V.
Si . .	70·00	69·85	62·70	69·10	65·42
C . .	30·00	29·80	32·26	30·20	27·93
Al_2O_3 / Fe_2O_3	—	—	0·93	0·46	5·09
CaO .	—	—	—	0·15	0·38
MgO .	—	—	0·11	—	0·21
	100·00	99·65	96·00	99·91	99·03

I. The calculated composition of SiC.
II. Moissan's pure product (Compt. rend. 1893, **117**, 425).
III. Commercial carborundum.
IV. Commercial carborundum purified by Mühlhaüser's method—heating in oxygen for 1 hour and treating with hot sulphuric and hydrofluoric acids (Dingl. poly. J. 1893, 289, 164).
V. Amorphous silicon carbide.

In the production of the silicon carbide in the furnaces, the inner granular core is surrounded by a layer of soft graphite which is succeeded by the crystallised carborundum and beyond this is a mass of "firesand."

Some modifications in the process have been

suggested. For example, Weber (U.S.P. 728528, 1903) proposed heating kaolin and coke in an electric furnace, whereby aluminium and silicon carbides are formed, and the former is decomposed by water and removed, leaving the carborundum behind. The production of a dense, compact variety, by the action of carbon and silicon on silicon carbide has been patented by the Carborundum Co. (U.S.P. 913324) and by Bouvier (F.P. 350369, 1904). Potter and Westinghouse (U.S.P. 875673, 1907) produce the carbide from silicon monoxide and carbon.

Articles may be formed in pure carbon and afterwards converted into carborundum by heating to a very high temperature in a bed of finely powdered carborundum or of sand and carbon (Bolling, B P. 6693, 1905).

Properties.—Carborundum crystallises in flat hexagonal rhombohedra having an adamantine lustre and a hardness of 9 5 For a detailed description of the crystalline structure of the three polymorphs of carborundum, *see* Ott (Z. Krist. 1925, 61, 515; 62, 201; 63, 1) It seems doubtful whether carborundum can scratch diamond, but it is used for drilling and polishing When pure the product is colourless, but the commercial product is greenish grey to yellow or blue, due to such impurities as iron, etc. Its sp gr. is 3 23 at 15° (Fitzgerald, J S.C.I. 1897, 16, 246).

It is infusible and quite unaffected up to a temperature of 2,220°C., when it is decomposed into silicon and graphitic carbon Acids have no effect upon it, but it is attacked by fused alkalis with the formation of a silicate and carbon. By this conversion into a silicate and precipitation of silica the silicon can be determined. The carbon is determined by oxidising the finely powdered material with lead chromate (Matthews, J S C.I. 1895, 14, 755; Mühlhauser, Z. anal. Chem. 1893, 32, 564).

Uses.—Carborundum was originally used in place of emery as an abrasive, and is still extensively employed as such. Though expensive, it does the work better and in one-third to a quarter of the time (Muhlhaüser, *l c*). The powder is used for glass cutting and grinding, and for polishing.

It is made up into grinding wheels, hones, etc., by mixing with moistened kaolin and felspar, moulding under hydraulic pressure, and firing the articles in a kiln for 7 days. Other binding materials, shellac, rubber, etc, are used for making grinding wheels for special purposes; and papers, similar to glass or emery paper, are made. The binding material may be dispensed with by moulding the carborundum, either crystalline or amorphous (part of it being ground to a very fine powder), with water and heating the articles to 2,500°F. in an oxidising flame. Oxidation causes the grains to cohere superficially and the method can be extended to coating other refractory articles (Carborundum Co., B.P. 9963, 1904; Tone, U.S.P. 772262, 1904).

Carborundum can be used instead of diamond for drill heads, if incorporated with a suitable metallic or ceramic matrix (Bouvier, F.P. 375338, 1907).

Neumann (Chem.-Ztg. 1900, 24, 1013) has shown that silicon carbide reduces the chlorides of silver, copper, nickel and lead to their respective metals, but it is obvious that for ordinary metals the usual reduction with carbon is certainly cheaper. By the action of silicon carbide on metallic oxides, many metallic silicides may be obtained. The reaction may be used for the preparation of special ternary and quaternary steels at a single operation (Muller and Baraduc, F.P. 361950, 1905; G.P. 210216, 1906).

Silicon carbide is used instead of ferro silicon as a source of silicon in steel making. Quantities of about 0 1–0 4% placed in the ladle, at regular intervals, dissolve in the molten metal and ensure solid castings (Kaufmann and Bouvier, F.P. 344906, 1904; Eng. and Min. J. 75, 481; F. J. Tone, "The Iron Age," New York, 1899).

One of the most important uses of carborundum is as a refractory material, for which its peculiar properties render it specially serviceable. Under the action of extreme heat, it does not, like many refractories, soften below the temperature of decomposition, 2,220°C., nor undergo after expansion nor after contraction, like silica and fireclay bricks. Its heat conductivity is higher than other refractories and its thermal expansion is low. It is extremely hard and resistant to abrasion and being chemically very inert resists the action of acids, slags, etc.

Carborundum articles can be made in various ways. The method of mixing water with a portion of the material in the form of a very fine powder gives a certain amount of binding power to the mass, and subsequent heating in an oxidising flame makes the article hard and compact (*cf. supra*). Bricks are also bonded with clay, but the amount of clay should be kept as small as possible, and the vitrification temperature of the clay should be high. Such bricks may be regarded as "clay-grog" bricks in which carborundum is substituted for grog, and this replacement, ranging from perhaps 10–65%, increases the tensile strength, thermal conductivity and slag resistance (Walton and Hauman, J. Amer. Ceram. Soc. 1930, 13, 935). Peters (*ibid.* 1922, 5, 181) found that the proportioning and sizing of the constituents was important and affected the tensile strength, the deformation under load and resistance to spalling. A very refractory and impermeable article can be made by mixing silicon carbide with not more than 25% of alumina, magnesia, lime, spinels, etc., and firing in an inert gas, such as carbon monoxide, nitrogen, helium, etc., to the point of incipient fusion of the bond. The heating should be rapid, to prevent recrystallisation of the carbide (Carborundum Co., Ltd, B.P. 419214, 8.5 33). In connection with the recrystallisation, Ruff suggests that it is "probably traceable to the temporary formation of a compound of carbon and oxygen, richer in carbon than CO" (Trans. Electrochem. Soc. 1935, 68, 87).

Carborundum firesand is the name given to a material obtained during the process of manufacture and is a compound of carbon and partially reduced silica. It is used as a refractory and when further heated in an electric furnace is converted into crystallised car-

borundum. It is a greyish-green, granular material, of sp.gr. 2·7, and can be bonded with fireclay and rammed into position as a solid mass, thus obviating the necessity of specially shaped blocks and eliminating joints in brickwork. It is largely used in high temperature furnaces, is very resistant to the scouring action of copper and brass slags, and can be applied as a protective coating to firebrick walls, and as the lining of ladles.

Two varieties of carborundum articles are made: *Refrax*, which consists of a dense mass of carborundum crystals (98–99%), bonded together by recrystallisation of the carbide; and *Carbofrax*, in which the crystals are bonded with a small percentage of a refractory clay. The properties of the two products are very similar, but the refractoriness and thermal conductivity are somewhat lower in the Carbofrax than the Refrax articles.

The following table summarises some of the main properties of carborundum refractories:—

Specific gravity	3·18
Apparent gravity . . .	2·3
Porosity	28%
Tensile strength	1,000–2,000 lb. per sq. in.
Crushing strength . . .	12,500–14,500 lb. per sq. in.
Specific heat 23°C. . . .	0·18
Thermal conductivity 100°C.	0·0275 g.-cals. per °C. per cm. cu. per sec.
Refrax, specific resistance of at 25°C.	50 ohms per c.c.
Refrax, specific resistance of at 1,400°C.	0·65 ohm. per c.c.
Carbofrax, specific resistance of at 25°C.	284,000 ohms per c.c.
Carbofrax, specific resistance of at 1,200°C.	40 ohms per c.c.
Linear expansion at 1,300°C.	0·6%

(Carborundum Co. Catalogues; *see also* Hartmann and Westmont, Trans. Amer. Electrochem. Soc. 1924, 46, 287; *ibid.* 1926, 50, 155; Hartmann and King, J. Amer. Ceram. Soc. 1926, 9, 758).

Owing to their properties, especially mechanical strength, high thermal conductivity, and resistance to all forms of chemical attack, carborundum refractories have been used for a great variety of boiler and other furnaces, for recuperator tubes, and for zinc and other retorts.

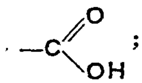
It may be mentioned that there are several similar materials, known by such names as *Silundum, Silfrax, Siloxicon* (Si_2C_2O) (E. G. Acheson, J.S.C.I. 1910, 29, 244), etc., formed by heating carbon and silica in an electric furnace, the composition of the products depending mainly on the ratio of the amounts of the raw materials treated and the extent to which the reduction of the silica is carried. *Crystolon* is the trade name of silicon carbide manufactured by the Norton Company of Worcester, Mass.

W. C. H.

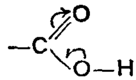
CARBOSERIN. Active charcoal prepared for internal use.

CARBOXIDE. A mixture of carbon dioxide and ethylene oxide used as a fumigant.

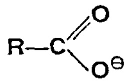
CARBOXYLIC ACIDS are characterised by the presence of the carboxyl group,



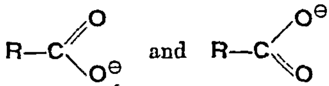
in this the carbonyl and hydroxyl groups are considerably modified in character, the acidic nature of the —OH group being markedly enhanced and the ketonic nature of the >CO group almost completely masked owing to polarisation in the sense



In fact, on modern views, the carboxyl ion is not to be regarded as



but rather as a resonance hybrid of the two forms



in which the charge is not localised on any one of the two oxygen atoms but must be regarded as being, statistically, equally divided between the two. The spatial arrangement of the atoms in the carboxyl group has been accurately worked out from X-ray data by Robertson and Woodward (J.C.S. 1936, 1817).

Systematically, carboxylic acids are named by using the suffixes "-oic acid" or "-carboxylic acid" or, occasionally, the prefix "carboxy-"; thus *n*-butyric acid,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

may be termed "butan-1-oic acid," "propane-1-carboxylic acid," or "1-carboxy-propane." The position of substituents is indicated either by Arabic numerals or Greek letters; in the former case, numbering is started with the carboxyl atom, but in the latter the carbon atom adjacent to the carboxyl group is the α-carbon atom:

$$CH_3 \ldots \underset{\beta}{\overset{3}{C}}H_2{\cdot}\underset{\alpha}{\overset{2}{C}}H_2{\cdot}\overset{1}{C}O_2H$$

This difference sometimes leads to confusion, the α-carbon atom being wrongly numbered 1.

Methods of Synthesis of Carboxylic Acids.—Synthetic methods fall into three groups, viz. the conversion of other groupings into the carboxyl group, the direct introduction of the carboxyl group, and methods involving condensation reactions; it will also be convenient to describe methods of introducing the cyano-group, since cyano-compounds are easily converted into carboxylic acids and form a very important source of the latter.

A. *The Conversion of Other Groupings into the Carboxyl Group.*—Carboxylic acids may be obtained by the oxidation of primary alcohols or of the corresponding aldehydes :

$$RCH_2{\cdot}OH \rightarrow RCHO \rightarrow RCO_2H$$

The most frequently used reagent for the oxidation of primary alcohols is alkaline potassium permanganate. Thus, in the preparation of *iso*butyric acid, a solution of 280 g. of potassium permanganate in $5\frac{1}{2}$ litres of water is added over 3–4 hours, with mechanical stirring and ice cooling, to a mixture of 100 g. of *iso*butyl alcohol and 300 c c. of water containing 30 g. of sodium carbonate. The product is allowed to attain room temperature over 12 hours, filtered, and the filtrate evaporated to small bulk. *iso*Butyric acid is isolated in 84% yield by extraction of the acidified solution with ether, followed by distillation (Fournier, Bull Soc. chim. 1909, [iv], 5, 920). A mixture of chromic and sulphuric acids may be used (Pierre and Puchot, Ann. Chim. 1873, [iv], 28, 75, 366), but this reagent has the disadvantage of giving rise to appreciable amounts of esters, acetals, etc. ; it may, in fact, be used for the preparation of carboxylic esters (*cf.* Robertson, Organic Syntheses, 1925, 5, 23). In some cases dilute nitric acid is a convenient oxidising agent (Mannich and Brose, Ber. 1923, 56, 835 ; Powell, Organic Syntheses, 1928, 8, 58).

In addition to the above reagents (*e g* potassium permanganate; Ruhoff, Organic Syntheses, 1936, 16, 39), aldehydes may be oxidised with alcoholic silver nitrate (Delépine and Bonnet, Compt. rend 1909, 149, 39), peracids (D'Ans and Kneip, Ber. 1915, 48, 1143), mercuric oxide (Blanchetière, Bull. Soc. chim 1923, [iv], 33, 345), and bromine water (Fischer and Hirschberger, Ber. 1889, 22, 3218), the last named being particularly useful in the sugar series (*cf.* Ling and Nanji, J.S C.I. 1922, 41, 28). With salts of nitrohydroxylamine, aldehydes yield hydroxamic acids which are readily hydrolysed by dilute acids ·

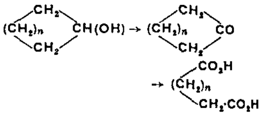
$$RCHO + NO_2{\cdot}NH\,OH \rightarrow RCO\,NH\,OH \xrightarrow{H_2O} RCOOH + NH_2{\cdot}OH$$

This affords a very smooth method *of oxidation* (Angeli and Angelico, Gazzetta, 1903, 33, II, 239).

The oxidation of methyl ketones to carboxylic acids may readily be carried out with sodium hypohalites :

$$RCO\,CH_3 + 3NaOX = RCO_2Na + CHX_3 + 2NaOH$$

This reaction, which is of very great importance in the field of terpene chemistry, is usually carried out by slow addition of the ketone to ice-cold sodium hypobromite, with violent agitation ; when the reaction is complete, the bromoform which separates is run off, excess hypobromite destroyed with sodium sulphite, and the acid obtained by acidification and extraction (*cf.* Baeyer, Ber. 1896, 29, 25 ; Wagner, *ibid.* 882 ; Sandborn and Bousquet, Organic Syntheses, 1928, 8, 108). The reaction has increased value in that it is applicable to unsaturated ketones (Einhorn, Annalen, 1888, 243, 363). The oxidation of cyclic ketones or alcohols is of importance for the preparation of dibasic acids :



It is usually carried out by dropping the ketone into nitric acid of suitable strength, which is heated initially to about 90° and then kept hot by the heat of the reaction ; the product is isolated by evaporation of the solution, but is liable to be contaminated by lower homologues owing to further oxidation (Bouveault and Locquin, Bull Soc. chim. 1908, [iv], 3, 437 ; Hentzschel and Wislicenus, Annalen, 1893, 275, 312 ; Thorpe and Kon, Organic Syntheses, 1925, 5, 9) ; aqueous potassium permanganate may also be used for this oxidation (J. von Braun and Lemke, Ber. 1922, 55, [B], 3529)

In the aromatic series, alkyl side-chains, especially if substituted, are readily oxidised to the carboxyl group, *e g* :

$$PhCH_2X \rightarrow PhCO_2H$$

Such oxidations are of particular importance for *purposes of orientation and are usually brought* about by refluxing with 2–5% potassium permanganate solution in the presence of sodium carbonate ; the precipitated " manganese mud " is filtered off and the acid liberated from the filtrate by acidification (Baeyer, Annalen, 1888, 245, 139 ; Clarke and Taylor, Organic Syntheses, 1930, 10, 20) Chromic acid has also been extensively used (*cf.* Clarke and Hartman, Organic Syntheses, 1922, 2, 95), while dilute nitric acid may be employed (Dittmar and Kekulé, Annalen, 1872, 162, 339), although this method suffers from the disadvantage that the product may be contaminated with nitration products. For a comparative study of such processes, *see* Law and Perkin, J.C S. 1907, 91, 261.

A method which is of use in certain special cases consists in the oxidation of unsaturated compounds :

$$RCH{:}CHR' \rightarrow RCO_2H + R'CO_2H$$

For preparative purposes alkaline potassium *permanganate is the reagent generally* employed (Saytzew, J. pr. Chem. 1886, [ii], 34, 304 ; Edmed, J.C S. 1898, 73, 627 ; Hill and McEwen, Organic Syntheses, 1933, 13, 4).

A very important process for the preparation of carboxylic acids is the hydrolysis of nitriles,

$$RCN \rightarrow RCO\,NH_2 \rightarrow RCO{\cdot}OH,$$

since these may be prepared by a wide variety of methods (*see below*). The hydrolysis may be carried out by refluxing with aqueous or alcoholic alkali until ammonia is no longer

evolved; the acid is then isolated from the acidified hydrolysis solution (Frankland and Kolbe, Annalen, 1848, **65**, 298; Adams and Marvel, J. Amer. Chem. Soc. 1920, **42**, 312; Read, Organic Syntheses, 1927, **7**, 54). It is frequently better to carry out the hydrolysis by refluxing with dilute acids (Städel, Ber. 1886, **19**, 1951; Robertson, Organic Syntheses, 1922, **2**, 59; Marvel and Tuley, *ibid.* 1925, **5**, 69; Clarke and Taylor, *ibid.* 1931, **11**, 96) and sometimes treatment with cold concentrated sulphuric acid followed by the addition of the equivalent of water may be used with advantage (Bruylants, Bull. Soc. chim. Belg. 1922, **31**, 229; 1924, **33**, 334; Linstead, Noble, and Boorman, J.C.S. 1933, 557). In difficult cases it is frequently convenient to hydrolyse with moderately concentrated sulphuric acid to the amide, which may then be converted into the acid by treatment with nitrous acid (Bouveault, Bull. Soc. chim. 1892, [iii], **9**, 368). The nitrile is heated to 120°–130° with 25–30 parts by weight of sulphuric acid for about an hour, the mixture is cooled, and the theoretical amount of concentrated aqueous sodium nitrite introduced; the mixture is stirred at 25° for some time and finally heated till the evolution of gas is complete, when it is poured into water, and the acid isolated by filtration or extraction (Sudborough, J.C.S. 1895, **67**, 602).

Two methods of obtaining carboxylic acids from ketones may be mentioned here. The well-known benzilic acid change:

$$PhCO{\cdot}COPh \rightarrow Ph_2C(OH)CO_2H$$

is brought about by alcoholic potash (Liebig, Annalen, 1838, **25**, 25; Adams and Marvel, Organic Syntheses, 1921, **1**, 33). Trialkylacetic acids are formed (as amides) by the fission of trialkylacetophenones by means of sodamide:

$$PhCO{\cdot}CR_3 + NaNH_2 + H_2O \rightarrow NH_2{\cdot}CO{\cdot}CR_3 + C_6H_6 + NaOH$$

(Haller and Bauer, Ann. Chim. 1913, [viii], **28**, 373).

B. *The Direct Introduction of the Carboxyl Group.*—The action of carbon monoxide on alkali hydroxides and alkoxides gives rise to carboxylic acids:

$$RONa + CO \rightarrow RCO{\cdot}ONa$$

This reaction is comparatively unimportant, the yields with the higher alkoxides being very poor (Poetsch, Annalen, 1883, **218**, 56); the method, however, finds technical application in the manufacture of formic acid (Geuther, Annalen, 1880, **202**, 317; G.P. 86419, 169730). Recently, Hardy (J.C.S. 1934, 1335; 1936, 358, 362) has studied the high pressure interaction of carbon monoxide and alcohols, yielding carboxylic acids.

A more important general method is the reaction of alkyl magnesium halides with carbon dioxide:

$$RMgX + CO_2 \rightarrow RCO{\cdot}OMgX$$
$$RCO{\cdot}OMgX + H_2O \rightarrow RCO_2H + Mg(OH)X$$

This reaction (Grignard, Ann. Chim. 1901, [vii], **24**, 435) is carried out by passing a stream of carbon dioxide into the Grignard reagent prepared in the usual manner; the complex is then broken up by treatment with dilute acid and the resulting carboxylic acid isolated by suitable methods. The reaction has found very wide application (*cf.* Meyer and Tögel, Annalen, 1906, **347**, 61; Gilman and Parker, Organic Syntheses, 1925, **5**, 73; Puntambeker and Zoellner, *ibid.* 1928, **8**, 104; Gilman, St. John and Schulze, *ibid.* 1931, **11**, 80). A similar reaction may be carried out with zinc alkyls (Schmitt, J. pr. Chem. 1890, [ii], **42**, 568).

Sodium alkyls also yield carboxylic acids with carbon dioxide:

$$RNa + CO_2 \rightarrow RCO_2Na$$

(Wanklyn, Annalen, 1858, **107**, 125; Ziegler and Schnell, *ibid.* 1924, **437**, 251). This reaction is particularly useful for the synthesis of acetylenic acids, since substituted acetylenes readily form sodio-derivatives, either without solvent or in ethereal solution; these sodio-derivatives give good yields of carboxylic acids on treatment with carbon dioxide (Faworsky, J. pr. Chem. 1888, [ii], **37**, 420; G.P. 132802).

The sodio-derivatives of alkylacetylenes also condense readily with ethyl chloroformate:

$$RC{:}CNa + ClCO_2Et \rightarrow RC{:}C{\cdot}CO_2Et + NaCl$$

(Moureu and Delange, Compt. rend. 1903, **136**, 552; G.P. 133631, 158252). Alkylmagnesium halides behave similarly (Houben, Ber. 1903, **36**, 3087) but their reaction with ethyl carbonate:

$$RMgX + CO(OEt)_2 \rightarrow XMgO{\cdot}CR(OEt)_2 \xrightarrow{H_2O} RCO{\cdot}OEt + EtOH + MgX(OH)$$

which generally gives very good yields, is to be preferred (Tschitschibabin, Ber. 1905, **38**, 561).

The Wurtz reaction between alkyl halides and chloroformic ester:

$$RCl + ClCO_2Et + 2Na = RCO_2Et + 2NaCl$$

(Wurtz, Annalen Suppl. 1860, **7**, 125; Fischer and Windaus, Ber. 1900, **33**, 1973) generally gives only poor yields; in the thiophen series, however, remarkably good yields have been recorded, *e.g.* the condensation of β-iodothiophen and ethyl chloroformate, using sodium amalgam, to give thiophen-β-carboxylic acid (Nähnsen, Ber. 1884, **17**, 2192).

A good method is the Friedel-Crafts reaction between aromatic hydrocarbons and urea chloride in the presence of aluminium chloride, yielding amides, which may readily be hydrolysed to the corresponding acids:

$$C_6H_6 + ClCO{\cdot}NH_2 \rightarrow C_6H_5{\cdot}CO{\cdot}NH_2 + HCl$$

(Gattermann, Annalen, 1888, **244**, 49). If the reaction is only to be carried out on a small scale, the urea chloride is prepared as required by heating cyanuric acid in a stream of dry hydrogen chloride and passing the gas into a carbon disulphide solution of the hydrocarbon containing aluminium chloride (Gattermann, Ber. 1899, **32**, 1117). By a similar process

phenyl *iso*cyanate in the presence of hydrogen chloride yields anilides:

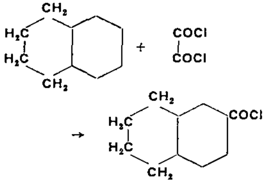
$$PhNCO + HCl \rightarrow PhNH\,COCl$$

$$C_6H_6 + PhNH{\cdot}COCl \rightarrow C_6H_5{\cdot}CO\,NHPh + HCl$$

(Leuckart, Ber. 1885, 18, 873; J. pr. Chem. 1890, [ii], 41, 301). Phosgene also condenses with aromatic hydrocarbons in the presence of aluminium chloride:

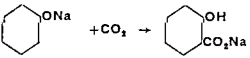
$$C_6H_6 + COCl_2 \rightarrow C_6H_5{\cdot}COCl + HCl$$

(Jacobsen, Ber. 1889, 22, 1220); the yields are, however, usually poor owing to further condensation with the production of ketones. It is of interest to note that tertiary bases condense with phosgene even in the absence of aluminium chloride to give the chlorides of the corresponding carboxylic acids (G.P. 44238). Replacement of phosgene by the less dangerous oxalyl chloride gives better yields; *e g.* tetralin with oxalyl chloride and aluminium chloride gives a 70% yield of *ar* tetrahydro β naphthoyl chloride:



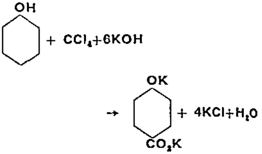
(J. von Braun, Kirschbaum and Schuhmann, Ber. 1920, 53, 1161).

Kolbe (J. pr. Chem 1874, [ii], 10, 94) discovered that sodium phenate, on heating in a stream of carbon dioxide, yields sodium salicylate:



The reaction may also be brought about by heating sodium phenyl carbonate in an autoclave at 130° (Schmitt, J. pr. Chem. 1885, [ii], 31, 397); at higher temperatures some *p*-hydroxybenzoic acid is formed. Other phenols behave similarly and with β naphthol suitable adjustment of the experimental conditions leads to the formation of the 1-, 3-, or 6 carboxylic acid (Morgan, J.S.C.I. 1931, 50, 104). Polyhydric phenols react more readily, the reaction being brought about by heating to 130° with *alkali bicarbonate solutions* (*Will and Albrecht*, Ber. 1884, 17, 2103; Kostanecki, Ber. 1885, 18, 3202; Thiele and Jaeger, Ber. 1901, 34, 2810). A further modification (Brunner, Annalen, 1907, 351, 319) consists in heating a glycerol solution of the polyhydric phenol with sodium bicarbonate in a stream of carbon dioxide.

The carboxyl group may also be introduced into phenols by a modified Reimer-Tiemann reaction, using carbon tetrachloride in place of chloroform:



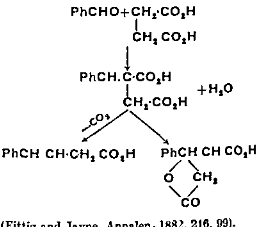
(Reimer and Tiemann, Ber. 1876, 9, 1285; Hasse, Ber. 1877, 10, 2185). This reaction generally yields the *p* carboxylic acid, whereas Kolbe's synthesis usually affords the *o* isomeride; copper or copper compounds have been recommended as catalysts (G.P. 258887).

C *Condensation Reactions.*—An important synthetic method for unsaturated acids is the Perkin reaction (Perkin, J C.S. 1877, 31, 389), which is brought about by heating an aromatic aldehyde with the salt of an acid in the presence of an acid anhydride:

$$RCHO + R'CH_2\,CO_2H \rightarrow RCH.CR'{\cdot}CO_2H + H_2O$$

Thus cinnamic acid is prepared by heating a mixture of 20 g. of benzaldehyde, 10 g. of fused sodium acetate, and 30 g. of acetic anhydride under an air-reflux for 8 hours at 180°; the mass is poured into sodium carbonate, unchanged benzaldehyde removed in steam, and cinnamic acid precipitated by acidification of the residual solution (Bertagnini, Annalen, 1856, 100, 126; Perkin, *l.c.*; Fittig, Ber. 1881, 14, 1826).

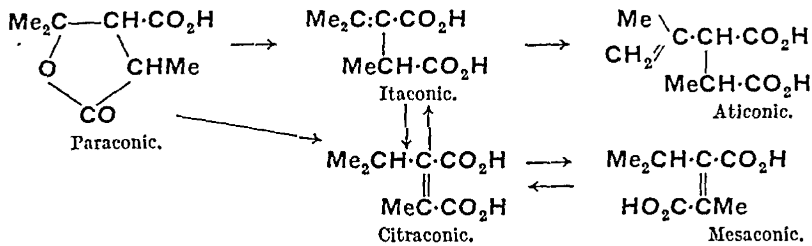
The reaction may be extended to acids of the succinic series but is then complicated by the formation of more than one product; thus benzaldehyde, sodium succinate, and acetic anhydride yield a mixture of phenylisocrotonic and phenylparaconic acids:



(Fittig and Jayne, Annalen, 1882, 216, 99).

Aliphatic aldehydes give very poor yields in the Perkin reaction but may be used successfully

for the preparation of alkylparaconic acids by Fittig's modification; the product may then be converted into the derived itaconic, citraconic, mesaconic, and aticonic acids:

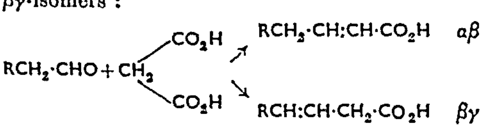


(Fittig, *et al.* Annalen, 1889, **255**, 1, 275; 1899, **304**, 117; 1899, **305**, 1). The paraconic acids also lose carbon dioxide on heating, with the formation of the corresponding monocarboxylic acid, $\beta\gamma$-unsaturated acids,

$$\mathrm{XYC{:}CH{\cdot}CHZ{\cdot}CO_2H}$$

(Jayne, Annalen, 1882, **216**, 113).

The Perkin reaction has also been extended to malonic acid. Thus, benzaldehyde, sodium malonate, and acetic anhydride react in the cold (Fittig, Ber. 1883, **16**, 1436) to give benzylidenemalonic acid, which is, however, better prepared by refluxing on the water-bath a mixture of benzaldehyde and malonic acid in acetic acid solution (Claisen and Crismer, Annalen, 1883, **218**, 315). The alkylidenemalonic acids so formed readily lose carbon dioxide on heating, yielding $\alpha\beta$-unsaturated acids. These reactions may be carried out in one stage using a wide variety of catalysts. Thus, acetaldehyde and malonic acid in acetic acid yield crotonic acid (Komnenos, Annalen, 1883, **218**, 149); if acetic anhydride is employed ketones may be brought into reaction, *e.g.* acetone and malonic acid yield $\beta\beta$-dimethylacrylic acid (Massot, Ber. 1894, **27**, 1225, 1574). Bases may also be used as catalysts; alcoholic ammonia brings about the condensation of benzaldehyde and malonic acid to cinnamic acid in good yield (Knoevenagel, Ber. 1898, **31**, 2604), but organic bases, such as primary and secondary amines (Knoevenagel, G.P. 97735, 156560, 161171), and pyridine (Verley, Bull. Soc. chim. 1899, **21**, 143; Doebner, Ber. 1900, **33**, 2140; Letch and Linstead, J.C.S. 1932, 455), are to be preferred. An extensive study of the base-catalysed reaction between aliphatic aldehydes and malonic acid has led to certain general conclusions; in the presence of large amounts of pyridine, $\alpha\beta$-unsaturated acids are formed exclusively, whereas small "catalytic" amounts of base, triethanolamine being by far the most convenient, give rise to the pure $\beta\gamma$-isomers:



(Boxer and Linstead, J.C.S. 1931, 740; Linstead, Noble, and Boorman, *ibid.* 1933, 557; *cf.* von Auwers, Annalen, 1923, 432, 58).

If cyanoacetic acid is used in place of malonic acid, α-cyano-$\alpha\beta$-unsaturated acids are formed (Fiquet, Ann. Chim. 1893, [vi], **29**, 433; Knoevenagel, G.P. 164296), and these may be decarboxylated by heating, giving rise to the unsaturated nitriles:

$$\mathrm{RCHO+CH_2(CN)CO_2H \rightarrow RCH{:}C(CN)CO_2H}$$
$$\downarrow$$
$$\mathrm{RCH{:}CH{\cdot}CN+CO_2}$$

or, by suitably adjusting the experimental conditions, both reactions may be carried out in one operation (Letch and Linstead, J.C.S. 1932, 450).

Aromatic aldehydes also yield carboxylic acids (as their esters) by condensation with esters; this method, which was discovered by Claisen (Ber. 1890, **23**, 976), is frequently superior to that of Perkin. Thus, benzaldehyde and ethyl acetate condense, without solvent, under the influence of sodium (wire or powder) to yield ethyl cinnamate:

$$\mathrm{PhCHO+CH_3{\cdot}CO_2Et \rightarrow PhCH{:}CH{\cdot}CO_2Et}$$

(Claisen, *l.c.*; Posner, J. pr. Chem. 1910, [ii], **82**, 435; Marvel and King, Organic Syntheses, 1929, **9**, 38). Both aldehydes and ketones react similarly with ethyl succinate in the presence of dry, alcohol-free, sodium ethoxide (Stobbe, Annalen, 1894, **282**, 283; 1899, **308**, 90; 1911, **380**, 1). Malonic ester reacts more readily than monobasic esters and also reacts with aliphatic aldehydes and ketones, thus enabling purely aliphatic unsaturated esters to be prepared by this method; as condensing agents, acetic anhydride (Claisen and Crismer, Annalen, 1883, **218**, 121; Meyenburg, Ber. 1895, **28**, 786) and ammonia, piperidine or diethylamine (Knoevenagel, Ber. 1898, **31**, 2593; Otterbacher, Organic Syntheses, 1930, **10**, 58), have been employed. With aliphatic aldehydes it is often a matter of great difficulty to prevent the reaction of 2 mols. of malonic ester with 1 of the aldehyde:

$$\mathrm{RCHO+CH_2(CO_2Et)_2}$$
$$\downarrow$$
$$\mathrm{R{\cdot}CH{:}C(CO_2Et)_2+H_2O}$$
$$\downarrow \mathrm{CH_2(CO_2Et)_2}$$
$$\mathrm{RCH{\cdot}CH(CO_2Et)_2}$$
$$\mathrm{|}$$
$$\mathrm{CH(CO_2Et)_2}$$

This reaction may be used for the preparation of glutaric acid and its β substituted derivatives (*cf.* Conrad and Guthzeit, Annalen, 1884, 222, 253; Knoevenagel, *Ber. 1914, 27, 2346*); *thus* an iced mixture of 32 g. of ethyl malonate and 8 g. of 40% aqueous formaldehyde is treated with 0 5 g of piperidine or diethylamine and then allowed to stand at room temperature in a *closed vessel for 12 hours, after which it is* heated on the water-bath for several hours. The oil is separated from the water and distilled (b p. 200°–205°/20 mm.). The 26 g. of $\alpha\gamma$-dicarbethoxyglutaric ester so obtained are *hydrolysed and decarboxylated by refluxing for* 6 hours with equal parts of concentrated hydrochloric acid and water; evaporation of the hydrolysis product yields glutaric acid.

Cyanoacetic ester may be condensed similarly *with aldehydes (Carrick, J. pr. Chem.* 1892, [ii], 45, 500), ketones (Komppa, Ber. 1900, 33, 3532) and β keto-esters (Linstead and Meade, J.C.S. 1934, 935; Barrett and Linstead, J.C.S. 1935, 440), the latter reaction being par*ticularly useful for the preparation of cyclic* dibasic acids. Ketones may similarly be condensed with acetoacetic ester (Merling and Welde, Annalen, 1909, 366, 131; Jupp, Kon, and Lockton, J.C.S. 1928, 1638) and ethyl oxalate *(cf.* Marvel and Dreger, Organic Syntheses, 1926, 6, 40).

Carbonyl compounds also react with α-bromoesters under the influence of zinc:

$$RR'CO + R''CHBr{\cdot}CO_2Et \rightarrow RR'CH(OH){\cdot}CHR''{\cdot}CO_2Et$$

(Reformatsky, Ber. 1887, 20, 1210; J. pr. Chem. 1896, [ii], 54, 469). This reaction was originally carried out without solvent; Lindenbaum (Ber. 1917, 50, 1270) introduced the use of benzene as solvent, a procedure which is now generally followed although toluene and xylene may be used if higher temperatures are desired. Zelinsky and Gutt (Ber. 1902, 35, 2140) used magnesium in ethereal solution, and Nieuwland and Daly (J. Amer. Chem. Soc. 1931, 53, 1842) recommended the use of copper powder as a catalyst enabling α-chloro esters to be used, but Kon and Nargund (J.C.S. 1932, 2461) in a general study found this to be unnecessary. The method has also been used successfully with β keto-esters (Linstead and Meade, J.C.S. 1934, 935; Chuang, Tien, and Huang, Ber. 1935, 68, [B], 864).

Dialkylglycollic esters are produced by the reaction of ethyl oxalate with alkyl magnesium halides:

$$\begin{matrix} CO_2Et \\ | \\ CO_2Et \end{matrix} + 2RMgX \rightarrow \begin{matrix} R_2C{\cdot}OH \\ | \\ CO_2Et \end{matrix}$$

(Grignard, Bull. Soc. chim. 1903, [iii], 29, 948). Keto-esters may be obtained by the reaction of acyl halides with bromo-esters in the presence of magnesium:

$$RCOBr + BrCH_2{\cdot}CO_2Et \rightarrow RCO{\cdot}CH_2{\cdot}CO_2Et$$

(Meyer and Togel, Annalen, 1906, 347, 71; Zeltner, Ber. 1908, 41, 589).

Geuther (Jahresberichte, *1863, 323)* found that 2 mols. of ethyl acetate condensed together under the influence of metallic sodium:

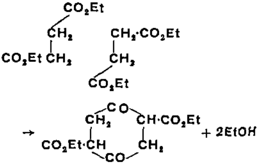
$$CH_3{\cdot}CO_2Et + CH_3{\cdot}CO_2Et \rightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et + EtOH$$

the β-ketonic ester, ethyl acetoacetate, being formed (*cf.* Wislicenus, Annalen, 1877, 186, 210; Snell and McElvain, J. Amer. Chem. Soc. 1931, 53, 750; Inglis and Roberts, Organic Syntheses, 1926, 6, 36). Higher homologues of ethyl acetate may be used (Hantzsch and Wohlbruck, Ber. 1887, 20, 1320; McElvain, J. Amer. Chem. Soc. 1929, 51, 3124) although the yields are usually poorer; according to Briese and McElvain (J. Amer. Chem. Soc. 1933, 55, 1697) better yields result if the reaction is carried out with sodium ethoxide under reduced pressure. Unlike esters may be employed, *e.g.* ethyl benzoate and ethyl acetate give ethyl benzoylacetate (Wahl and Doll, Bull. Soc. chim. 1913, [iv], 13, 265), ethyl formate and other esters yield formyl esters:

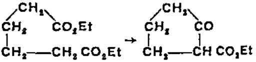
$$H{\cdot}CO_2Et + R{\cdot}CH_2{\cdot}CO_2Et \rightarrow R{\cdot}HC\begin{matrix} \diagup CHO \\ \diagdown CO_2Et \end{matrix}$$

(Wislicenus, Annalen, 1908, 363, 347; Wheeler and McFarland, *Amer. Chem. J. 1910, 43, 22)*

Similar reactions may be brought about with dibasic esters. Ethyl succinate condenses with itself in the presence of sodium, yielding a *cyclo*hexane derivative:



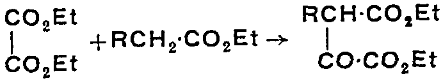
(Herrmann, Annalen, 1882, 211, 306). Esters of *the adipic, pimelic, and suberic series* undergo ring-closure in the presence of sodium, yielding cyclic β keto-esters:



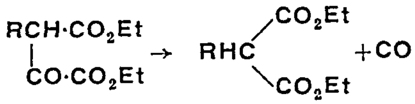
The reaction is usually carried out by adding 1 g. mol. of the ester to 1 g. atom of sodium powder under benzene; the reaction is completed by heating on the water-bath until all the sodium is used up, a hard cake of sodio-derivative usually filling the flask. This is decomposed with dilute acid and the ester present in the benzene layer is worked up *in* the usual way (Dieckmann, Annalen, 1901, 317, 27; Linstead and Meade, J.C.S. 1934, 940). The reaction gives negligible yields with esters of the glutaric, sebacic, and azelaic series.

The condensation of ethyl oxalate with esters,

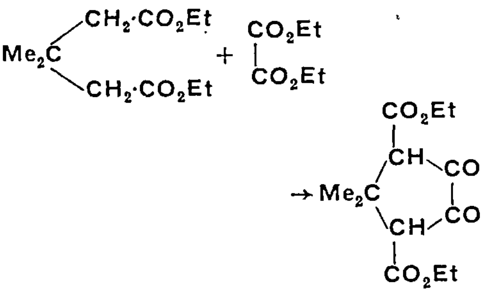
is of great importance since the α-keto-esters first formed



lose carbon monoxide on heating with the production of malonic esters :

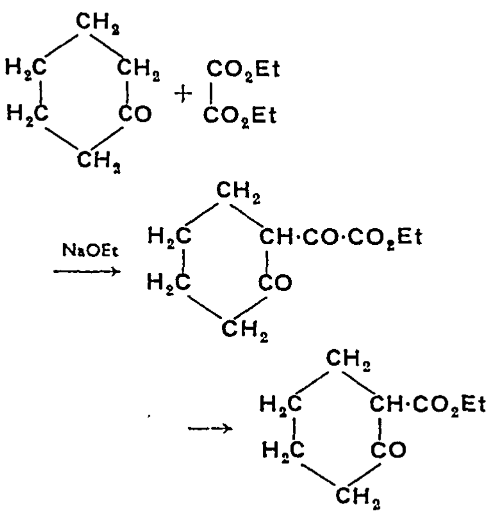


(Wislicenus, Annalen, 1888, **246**, 316 ; Ber. 1894, **27**, 1093) ; the reaction affords a convenient method of preparing phenylmalonic esters which are not accessible by direct alkylation of malonic ester (Levene and Meyer, Organic Syntheses, 1936, **16**, 33). With dibasic esters under drastic conditions cyclic products are formed (Dieckmann, Ber. 1897, **30**, 1470), the following well-known example being the basis of Komppa's synthesis of camphor :

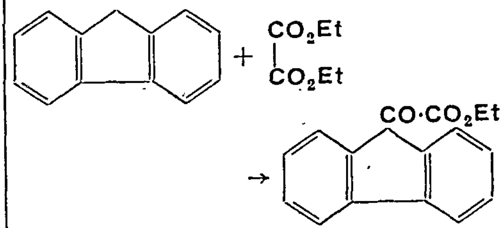


(Komppa, Annalen, 1909, **368**, 126).

The condensation of ethyl oxalate with cyclic ketones is of importance, since it affords a ready method of obtaining the reactive *cyclo*hexanone-β-carboxylic esters :



The condensation is carried out using ice-cold sodium ethoxide, and the crude *cyclo*hexanone-β-oxalic ester on vacuum distillation yields the β-keto-ester directly (Kötz and Michels, Annalen, 1906, **350**, 210 ; Kötz, *ibid.* 1908, **358**, 198 ; Ruzicka, Koolhaas and Wind, Helv. Chim. Acta, 1931, **14**, 1163). If is of interest to note that the methylene group of fluorene is sufficiently reactive to undergo a similar condensation :



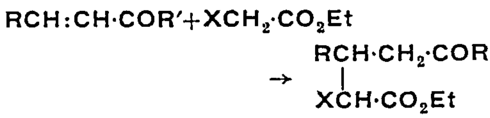
(Thiele, Ber. 1900, **33**, 666, 851 ; Wislicenus, Annalen, 1924, **436**, 1).

Ethyl carbonate may be condensed with nitriles under the influence of sodamide, the reaction affording a method of preparing otherwise inaccessible arylcyanoacetic esters :

$$PhCH_2{\cdot}CN + CO(OEt)_2 \rightarrow PhCH(CN)CO_2Et + EtOH$$

(*cf.* Nelson and Cretcher, J. Amer. Chem. Soc. 1928, **50**, 2758).

αβ-Unsaturated esters and ketones under the influence of sodium ethoxide or bases combine additively with malonic, acetoacetic and cyanoacetic esters :

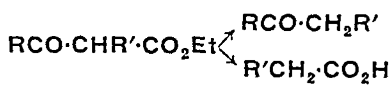


(Michael, J. pr. Chem. 1887, [ii], **35**, 349 ; Auwers, Ber. 1891, **24**, 307 ; Michael, J. pr. Chem. 1894, [ii], **49**, 20 ; Vorländer, Ber. 1894, **27**, 2053) ; the Michael reaction is very important for the synthesis of substituted glutaric and tricarballylic acids (*cf.* Clarke and Murray, Organic Syntheses, 1925, **4**, 29).

The special importance of the reactions described above, leading to the production of β-keto-esters, lies in the fact that their sodio-derivatives are readily alkylated :

$$RCO{\cdot}CH_2{\cdot}CO_2Et + R'X \rightarrow RCO{\cdot}CHR'{\cdot}CO_2Et$$

The products may then be easily hydrolysed yielding, according to the reagent employed, ketones or acids :



For the monoalkylation of acetoacetic ester, 1 g. mol. of the ester is added to a solution of sodium ethoxide prepared from 1 g. atom of sodium and 10 parts by weight of absolute alcohol ; the alkyl halide is added cautiously and the reaction, which proceeds with precipitation of sodium halide, completed by heating on the water-bath until the solution is no longer alkaline (Wislicenus, Annalen, 1877, **186**, 216 ; Brühl, J. pr. Chem. 1894, [ii], **50**, 133 ; Marvel and Hager, Organic Syntheses, 1927, **7**, 36). Aryl halides cannot be used in this reaction, but halogenated esters react readily (Emery, Ber. 1891, **24**, 283 ; Bone and Sprankling, J.C.S.

1899, 75, 839; Adkins, Isbell, and Wojcik, Organic Syntheses, 1934, 14, 38). Methylation can also be carried out with dimethyl sulphate (Grandmougin, Havas, and Guyot, Chem.-Ztg. 1913, 37, 812). The mono alkyl derivatives so formed may be further alkylated by similar methods (Conrad and Limpach, Annalen, 1878, 192, 153). Pulverised ("molecular") sodium in inert solvents may sometimes advantageously replace sodium ethoxide in these condensations. As usually prepared the lower mono-alkylacetoacetic esters are contaminated with unalkylated and di alkylated material; they may be purified by a process of partial hydrolysis (Michael and Wolgast, Ber. 1909, 42, 3176).

Acyl halides undergo similar condensations with acetoacetic ester, but the products usually contain some O acyl derivative of the enolic form; however, careful control of the conditions enables good yields of the desired diketo-ester to be obtained.

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et + RCOCl \rightarrow \begin{matrix} CH_3{\cdot}CO \\ RCO \end{matrix} > CH{\cdot}CO_2Et$$

(Claisen, Annalen, 1896, 291, 71); the resulting diketo esters cannot be further alkylated. Calcium carbide has been recommended in place of sodium in such reactions (Packendorff, Ber. 1931, 64, [B], 948). Acetoacetic ester also condenses readily with aldehydes, yielding alkylideneacetoacetic esters (Knoevenagel, Ber. 1898, 31, 2773, 1896, 29, 172).

As mentioned above, the importance of the *alkylated acetoacetic esters lies in their fission* to other products. This takes place in two ways The so-called "ketonic fission"

$$R{\cdot}CO{\cdot}CR'R''{\cdot}CO_2Et + H_2O \rightarrow R{\cdot}CO{\cdot}CHR'R'' + CO_2 + EtOH$$

is effected by refluxing with dilute mineral acids (Conrad, Annalen, 1877, 188, 222; Fittig and Wolff, *ibid.* 1882, 216, 127; Emery, *ibid.* 1897, 295, 94; Johnson and Hager, Organic Syntheses, 1927, 7, 60); it is of importance for the synthesis *of keto acids Of greater importance for the* synthesis of carboxylic acids is the "acid fission":

$$RCO{\cdot}CR'R''{\cdot}CO_2Et + H_2O \rightarrow RCO_2H + CHR'R''{\cdot}CO_2H$$

which is effected by refluxing with concentrated alkali (Kiliani, Ber. 1886, 19, 227; Fittig and Messerschmidt, Annalen, 1881, 208, 92). A variant is the "ester fission":

$$RCO{\cdot}CR'R''{\cdot}CO_2Et + EtOH \rightarrow RCO_2Et + CHR'R''{\cdot}CO_2Et$$

in which alcoholic sodium ethoxide (Dieckmann, Ber. 1900, 33, 2670, 2681; 1908, 41, 1260, 1266) or 1:8 naphthylenediamine hydrochloride (Sachs, Annalen, 1909, 365, 74) is the hydrolysing agent.

In a precisely analogous manner malonic ester can be alkylated, sodium ethoxide and alkyl halides generally being employed for this purpose (Conrad, Annalen, 1880, 204, 127, 134; Adams and Kamm, Organic Syntheses, 1925, 4, 11); alkyl sulphates may also be used (Grandmougin, Havas, and Guyot, Chem. Ztg 1913, 37, 812; Hurd, Jones, and Blunck, J. Amer. Chem. Soc. 1935, 57, 2034) and magnesium may sometimes advantageously replace sodium (Lund, Ber. 1934, 67, [B], 935), particularly with acyl halides. As in the case of acetoacetic ester, aryl halides do not react, but halogenated esters react readily (Bischoff, Annalen, 1882, 214, 53); in certain cases, however, the reaction takes an unexpected course, thus:

$$Me_2CBr{\cdot}CO_2Et + MeCH(CO_2Et)_2 \longrightarrow \begin{matrix} MeCH{\cdot}CO_2Et \\ | \\ CH_2 \\ | \\ MeC(CO_2Et)_2 \end{matrix}$$

(Bone and Sprankling, J.C.S. 1899, 75, 839; Rydon J.C.S. 1936, 1444). Cyanoacetic ester can replace malonic ester in all these reactions (Haller, Compt. rend 1887, 104, 1626; Bone and Sprankling, J C.S. 1900, 77, 654; Zelinsky, Ber. 1888, 21, 3165). As usually prepared the lower alkylmalonic esters are contaminated with dialkylated and unalkylated material, they may be purified by a process of partial hydrolysis (Michael, J. pr. Chem. 1905, [ii], 72, 547, 550)

For synthetic purposes the alkylmalonic esters are hydrolysed to the alkylmalonic acids with aqueous or alcoholic alkali (Conrad, Annalen, 1880, 204, 132; Conrad and Bischoff, *ibid* 1880, 204, 168, Bischoff and Siebert, *ibid* 1887, 239, 92). The alkylmalonic acids are decarboxylated to monobasic acids on heating above their melting-point until the evolution of gas ceases:

$$RCH(CO_2H)_2 \rightarrow RCH_2{\cdot}CO_2H + CO_2$$

(*l.c.*; Krafft, Ber. 1884, 17, 1630). Hydrolysis and decarboxylation may be carried out in one operation by refluxing with dilute mineral acids (Komppa, Ber. 1900, 33, 3530; Knoevenagel, Ber. 1894, 27, 2346; Vliet, Marvel, and Hsueh, Organic Syntheses, 1931, 11, 76), this procedure is particularly useful in the *synthesis of polybasic acids (cf. Clarke and* Murray, Organic Syntheses, 1925, 4, 77); in difficult cases the use of a mixture of water, formic acid, and sulphuric acid is advantageous (*cf.* Rydon, J.C.S. 1936, 595). In those syntheses in which acetoacetic ester or malonic ester may be employed to prepare the same material, the malonic ester method is to be preferred, as the yields are usually better.

A method for the synthesis of dicarboxylic acids is afforded by the elimination of 2 atoms of bromine from 2 mols. of a bromomonocarboxylic ester under the influence of finely divided silver:

$$2RCHBr{\cdot}CO_2Et + 2Ag \rightarrow \begin{matrix} RCH{\cdot}CO_2Et \\ | \\ RCH{\cdot}CO_2Et \end{matrix} + 2AgBr$$

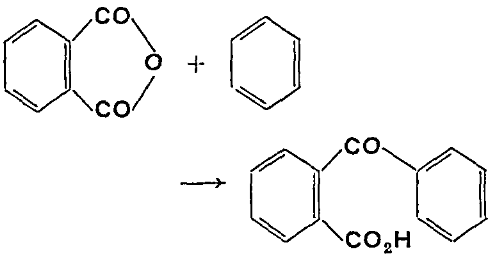
(Wislicenus, Annalen, 1869, 149, 220; Auwers, *ibid.* 1896, 292, 167; Hell and Rothberg, Ber. 1889, 22, 60); the yields are, however, usually poor and rearrangements often occur.

Copper powder has been employed for the same purpose (Ince, J.C.S. 1848, 1, 157).

Cyclic keto-acids may be obtained by the Friedel-Crafts reaction between acyl halides and acids :

$$PhCOCl + PhCO_2H \rightarrow PhCO{\cdot}C_6H_4{\cdot}CO_2H$$

Better results are obtained using acid anhydrides in place of acyl halides :



(H. von Pechmann, Ber. 1880, **13**, 1612 ; Burcker, Ann. Chim. 1882, [v], **26**, 435, 449) ; this reaction has been much used in recent years (Groggins and Nagel, Ind. Eng. Chem. 1934, **26**, 1313 ; Somerville and Allen, Organic Syntheses, 1933, **13**, 12 ; Fieser and Hershberg, J. Amer. Chem. Soc. 1936, **58**, 2315).

An important method for the synthesis of $\beta\beta$-dialkylglutaric acids is the condensation of ketones with cyanoacetic ester (Guareschi, Atti R. Accad. Sci. Torino, 1900–1901, **36**, 443; Kon and Thorpe, J.C.S. 1919, **115**, 693). The reaction is carried out by allowing a mixture of the ketone and ethyl cyanoacetate to stand at 0° with saturated alcoholic ammonia for some days; the precipitated ammonium salt is then filtered off and converted into the imide with hydrochloric acid; this is then hydrolysed and decarboxylated by heating with sulphuric acid (Vogel, J.C.S. 1934, 1760):

$$RR'CO + 2CH_2(CN)CO_2Et$$
$$\downarrow$$
$$RR'C\left\langle\begin{matrix}CH(CN)CO\\CH(CN)CO\end{matrix}\right\rangle NH$$
$$\downarrow$$
$$RR'C\left\langle\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}\right.$$

A convenient method of preparing $\alpha\alpha$-dialkylsuccinic acids is the condensation of cyanohydrins with cyanoacetic ester, which is carried out with sodium ethoxide (Higson and Thorpe, J.C.S. 1906, **89**, 1465). Acid hydrolysis of the product yields the desired succinic acid :

$$RR'C(OH)CN + CH_2(CN)CO_2Et$$
$$\downarrow$$
$$RR'C(CN){\cdot}CH(CN)CO_2Et$$
$$\downarrow$$
$$\begin{matrix}RR'C{\cdot}CO_2H\\ |\\ CH_2{\cdot}CO_2H\end{matrix}$$

D. *Introduction of the Cyano-Group.*—The cyano-group is of importance as a precursor of the carboxyl group, into which it is readily converted by hydrolysis. It is, perhaps, most readily introduced by the interaction of halogen compounds with alkali cyanides :

$$RX + NaCN \rightarrow NaX + RCN$$

This reaction is generally carried out by refluxing in alcoholic solution, but a wide variety of procedure has been described (*cf.* Rosenmund and Struck, Ber. 1919, **52**, [B], 1749 ; Adams and Thal, Organic Syntheses, 1922, **2**, 9 ; Kohler and Allen, *ibid.* 1923, **3**, 53 ; Marvel and McColm, *ibid.* 1925, **5**, 103 ; Inglis, *ibid.* 1928, **8**, 74 ; Ruhoff, *ibid.* 1936, **16**, 35). The action of cuprous cyanide on allyl alcohol and hydrochloric acid has been used with great success (Breckpot, Bull. Soc. chim. Belge, 1930, **39**, 465). Nitriles are also obtained by heating the salts of sulphonic acids with potassium cyanide (Merz and Mülhäuser, Ber. 1870, **3**, 710).

Hydrogen cyanide may be added directly to $\alpha\beta$- double bonds in unsaturated acids, esters, nitriles, and ketones, a little alkali or organic base being employed as a catalyst,

$$RCH{:}CHX + HCN \rightarrow RCH(CN)CH_2X$$

(Bredt and Kallen, Annalen, 1896, **293**, 350; Claus, *ibid.* 1878, **191**, 33; Lapworth, *et al.* J.C.S. 1904, **85**, 1214; 1922, **121**, 49, 1699; Organic Syntheses, 1928, **8**, 88). A similar reaction takes place with the carbonyl groups of aldehydes and ketones thus yielding cyanohydrins :

$$RR'CO + HCN \rightarrow RR'C(OH)CN$$

(Ultée, Rec. trav. chim. 1909, **28**, 1, 248, 257 ; Jones, J.C.S. 1914, **105**, 1560 ; Lapworth and Manske, J.C.S. 1928, 2533 ; 1930, 1976). It is generally best to add a slight excess of liquid hydrogen cyanide to the carbonyl compound with a little potassium cyanide, caustic alkali or secondary amine as catalyst ; sometimes, however, hydrogen cyanide produced *in situ* from potassium cyanide and an acid gives equally good results (*cf.* Ruzicka and Brugger, Helv. Chim. Acta, 1926, **9**, 399 ; Welch and Clemo, J.C.S. 1928, 2629 ; Boorman and Linstead, J.C.S. 1935, 261 ; Cox and Stormont, Organic Syntheses, 1935, **15**, 1). Another method consists in treating the bisulphite compound of the carbonyl compound with aqueous potassium cyanide (Bucherer and Grolée, Ber. 1906, **39**, 1224 ; Albert, Ber. 1916, **49**, 1382 ; Corson, Dodge, Harris, and Yeaw, Organic Syntheses, 1926, **6**, 58). Cyanohydrins may be obtained from almost all carbonyl compounds and since they may be dehydrated to unsaturated nitriles and these latter reduced to saturated compounds their synthetic importance is very great ; for recent examples of their employment in this way *see* Hückel and Lampert, Ber. 1934, **67**, [B], 1811 ; Rydon, J.C.S. 1937, 257. A similar reaction with ammonium cyanide is useful for the synthesis of α-amino-acids :

$$RR'CO + NH_4{\cdot}CN \rightarrow RR'C(NH_2)CN$$

(Zelinski and Stadnikoff, Ber. 1906, 39, 1725; 1908, 41, 2063). The dehydration of aldoximes.

$$RCH{:}NOH \rightarrow RCN + H_2O$$

has also been used for the preparation of nitriles (*cf.* Buck and Ide, Organic Syntheses, 1935, 15, 85).

In the aromatic series, important methods for the preparation of nitriles are the reactions of Sandmeyer and Gattermann. The latter (Ber. 1890, 23, 1218) consists in treating a diazonium cyanide with copper bronze. In the former (Ber. 1884, 17, 1633, 2650), which is generally more convenient for the preparation of nitriles (*cf.* Clarke and Read, Organic Syntheses, 1925, 4, 69), the diazonium chloride is treated with cuprous cyanide and then warmed.

Reactions of Carboxylic Acids—(i) *Salt Formation*—The salts of carboxylic acids may be obtained by neutralisation of the free acid with the appropriate hydroxide or carbonate. Salts of the alkali metals are generally prepared by careful neutralisation, followed by evaporation, salts of the alkaline earths and heavy metals, by boiling with an aqueous supension of the metallic carbonate, followed by filtration and evaporation. Sparingly soluble salts may be obtained by double decomposition, the preparation of silver salts is usually so carried out by adding aqueous silver nitrate to an aqueous solution of the ammonium salt of the acid, the precipitated silver salt being filtered off and dried.

(ii) *Preparation of Acyl Halides.*—For the preparation of acyl chlorides phosphorus pentachloride, phosphorus trichloride, and thionyl chloride are the most widely used reagents, the choice being largely dependent on the properties of the acyl chloride. If phosphorus pentachloride is used, phosphorus oxychloride is an end product of the reaction:

$$RCO_2H + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

If the acyl chloride has a boiling-point widely different from that of phosphorus oxychloride it may be separated by distillation (Gräbe and Bungener, Ber. 1879, 12, 1079, Krafft and Burger, Ber 1884, 17, 1378; Adams and Jenkins, Organic Syntheses, 1923, 3, 75); if this method is not applicable, treatment with light petroleum may be used to separate the inorganic material (Wallach, Ber. 1875, 8, 300). It is frequently desirable to employ diluents, such as benzene or chloroform (Gräbe, Annalen, 1896, 291, 10), in the cases of acids that are slow to react, phosphorus oxychloride, used as solvent, facilitates the reaction (H. von Pechmann, Annalen, 1891, 264, 282; Pschorr, Ber. 1898, 31, 1295).

If the acyl chloride has a low boiling point, phosphorus trichloride is a better reagent:

$$3RCO_2H + PCl_3 \rightarrow 3RCOCl + HPO_3$$

since the phosphorous acid formed is non-volatile. The use of phosphorus halides is attended by the danger of contamination of the product with phosphorus compounds, which may be very difficult to remove completely. For this reason thionyl chloride is frequently used; the reaction proceeds in the cold and is finished by gentle warming and has the advantage that all the inorganic products are gases:

$$RCO_2H + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$

(Meyer, Monatsh. 1901, 22, 109, 415, 777; Herre, Ber. 1895, 28, 594; Helferich and Schaefer, Organic Syntheses, 1929, 9, 32). With this reagent, however, succinic, glutaric, and maleic acids form, not acyl chlorides, but anhydrides (McMaster and Ahmann, J. Amer. Chem. Soc. 1928, 50, 145), in some cases the presence of pyridine is necessary for the reaction to proceed (Carre and Libermann, Compt. rend. 1934, 199, 1422).

Acyl chlorides may also be obtained by the action of phosphorus oxychloride on the sodium salts of carboxylic acids:

$$2RCO_2Na + POCl_3 \rightarrow 2RCOCl + NaPO_3 + NaCl$$

(Gerhardt and Chiozza, Compt. rend. 1853, 36, 655, Rugheimer and Hofmann, Ber. 1884, 17, 739, Rupe, Annalen, 1909, 369, 331). On the technical scale phosphorus oxychloride (G P. 163103, 171787), phosgene (G.P. 29669), sulphuryl chloride and chlorosulphonic acid (G.P. 63593, 161882), and a mixture of sulphur dioxide and chlorine (G P. 210805) have found application. The use of silicon tetrachloride has also been proposed (Montonna, J. Amer Chem. Soc 1927, 49, 2114). Clark and Bell (Trans. Roy Soc. Canada, 1933, [iii], 27, III, 97) made a general survey of methods of preparing acyl chlorides and concluded that thionyl chloride was the most satisfactory reagent for the process.

Acyl bromides are obtained analogously using bromides of phosphorus (Claisen, Ber. 1881, 14, 2474) or, more simply, red phosphorus and bromine (Gal, Annalen, 1864, 129, 53). Acyl iodides cannot be obtained directly from carboxylic acids but are prepared by the action of phosphorus iodide on the anhydrides or salts or from the acyl chlorides with calcium iodide (Guthrie, Annalen, 1857, 103, 335; Spindler, *ibid.* 1885, 231, 272). Acyl fluorides are obtained from the chlorides with zinc or silver fluoride (Borodin, Annalen, 1863, 126, 60; Guenez Bull. Soc. chim. 1891, [iii], 5, 886) or by the interaction of fluorosulphonic acid or a salt with the free acid or one of its salts:

$$RCO_2X + XFSO_3 \rightarrow RCOF + X_2SO_4$$

(Traube and Krahmer, Ber. 1919, 52, [B], 1296). Recently the use of potassium fluoride and benzoyl chloride has been recommended (Nesmejanov and Kahn, Ber. 1934, 67, [B], 370).

(iii) *Preparation of Acid Anhydrides.*—The most convenient method for the preparation of acid anhydrides consists in refluxing the acid with acetyl chloride or acetic anhydride, followed by distillation (Anschütz, Annalen, 1884, 226, 1; Autenrieth, Ber. 1901, 34, 186; Fournier, Bull. Soc. chim. 1909, [iv], 5, 922; Clarke and Rahrs, Organic Syntheses, 1923, 3, 21); when acetic anhydride is employed the use of catalysts such as pyridine, sulphuric acid, or hydrogen chloride enables the reaction to be carried out below 100° (G.P. 442221). In the case of stereo isomeric dicarboxylic acids it is usually, although not

always, the *cis*-acid which yields an anhydride readily by the above methods, the *trans*-acid being converted into the *cis*-anhydride on heating in sealed tubes with acetyl chloride or acetic anhydride to high temperatures; phosphorus oxychloride has been used to prepare anhydrides of dibasic acids (*cf.* Shriner and Struck, Organic Synthesis, 1932, **12**, 66).

A general method and, incidentally, the classical method, is the slow distillation of the acyl chloride with the sodium salt :

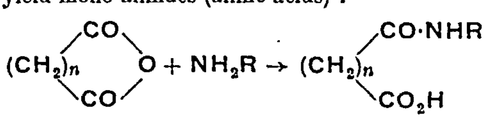
$$RCOCl+RCO{\cdot}ONa \rightarrow RCO{\cdot}O{\cdot}COR+NaCl$$

(Gerhardt, Annalen, 1853, **87**, 65, 149). In technical practice the method is simplified by treating the sodium salt with sufficient phosphorus oxychloride, phosphorus trichloride, thionyl chloride, or sulphuryl chloride to convert one half of the salt to the acid chloride ; the mixture is then distilled (Denham and Woodhouse, J.C.S. 1913, **103**, 1861 ; G.P. 163103, 171787, 29669, 63593, 161882, 210805). Acid anhydrides may also, in certain cases, be obtained by treatment of acyl halides with tertiary bases such as pyridine or quinoline (Wedekind, Ber. 1901, **34**, 2070 ; G.P. 117267).

(iv) *Preparation of Amides, Imides, Etc.*—A general method for the preparation of amides is the reaction of the acyl chloride with ammonia :

$$RCOCl+NH_3 \rightarrow RCO{\cdot}NH_2+HCl$$

(Liebig and Wöhler, Annalen, 1832, **3**, 268). For the preparation of small amounts of amide it is unnecessary to isolate the acyl chloride ; the acid is simply treated with thionyl chloride and the reaction product added to concentrated aqueous ammonia with cooling (Aschan, Ber. 1898, **31**, 2344). In the preparation of substituted amides (anilides, etc.) it is better to employ benzene or ether as a diluent (*cf.* Franzen, Ber. 1909, **42**, 2465). A similar reaction takes place with anhydrides (Autenrieth Ber. 1901, **34**, 186), but this is, in general, only valuable in the case of dibasic acids, which yield mono-anilides (anilic acids) :



(Anschütz, Ber. 1887, **20**, 3214 , 1888, **21**, 88 ; Annalen, 1890, **259**, 137 ; Auwers, *ibid.* 1895, **285**, 225) ; here again the reaction with amines is generally carried out in a neutral solvent such as benzene.

The oldest method for obtaining amides is by the distillation of the ammonium salt of the acid :

$$RCO_2NH_4 \rightarrow RCO{\cdot}NH_2+H_2O$$

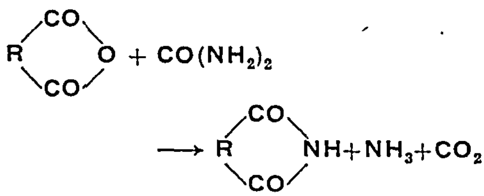
Thus acetamide is prepared by refluxing a mixture of 100 g. of ammonium acetate with 120 g. of acetic acid for 5 hours and distilling the product (Dumas, Ann. Chim. 1830, [ii], **44**, 130 ; Hofmann, Ber. 1882, **15**, 981 ; François, J. Pharm. Chim. 1906, [vi], **23**, 230 ; Noyes and Goebel, J. Amer. Chem. Soc. 1922, **44**, 2294 ; Coleman and Alvarado, Organic Syntheses, 1923, **3**, 3). This process is also satisfactory for the preparation of the imides of dibasic acids (*cf.* Clarke and Behr, Organic Syntheses, 1936, **16**, 75). Anilides, etc., may be prepared in a similar manner by refluxing a mixture of the acid and the amine until the water has been driven off (*cf.* Dunlap, J. Amer. Chem. Soc. 1902, **24**, 758 ; Webb, Organic Syntheses, 1927, **7**, 6).

Many esters yield amides by treatment in the cold with concentrated aqueous ammonia :

$$RCO_2R'+NH_3 \rightarrow RCO{\cdot}NH_2+R'OH$$

(Fischer and Dilthey, Ber. 1902, **35**, 844 ; Meyer, Monatsh. 1906, **27**, 31 ; Jacobs and Heidelberger, Organic Syntheses, 1927, **7**, 16 ; Corson, Scott, and Vose, *ibid.* 1929, **9**, 36 ; *cf.* Chattaway, J.C.S. 1936, 355) ; in the case of inert esters good results are sometimes obtained by heating the ester with concentrated alcoholic ammonia in a sealed tube at 100°–150° (Hofmann, Ber. 1882, **15**, 977). This method has also been applied to the preparation of hydrazides, using hydrazine hydrate (Curtius, *et al.* J. pr. Chem. 1895, [ii], **51**, 165, 180, 295, 353 ; 1901, [ii], **64**, 401, 419), and of hydroxamic acids, using hydroxylamine (Schroeter, Ber. 1898, **31**, 2191) in place of ammonia.

Dibasic acids may be converted into their imides by heating their ammonium salts or monoamides (Laurent, Annalen, 1842, **41**, 110 ; Febling, *ibid.* 1844, **49**, 196) or by treatment of their chlorides or anhydrides with ammonia (Kuhara, Amer. Chem. J. 1881, **3**, 29) ; a convenient process for small quantities consists in heating the anhydride with urea :



(Laurent, Ann. Chim. 1836, **19**, 47 ; Herzog, Z. angew. Chem. 1919, **32**, 301) or with ammonium carbonate (*cf.* Noyes and Porter, Organic Syntheses, 1922, **2**, 75).

(v) *Preparation of Nitriles.*—The preparation of nitriles from carboxylic acids is generally carried out through the amide, which is readily dehydrated,

$$RCO{\cdot}NH_2 \rightarrow RCN+H_2O,$$

by heating with phosphorus pentoxide (Dumas, Annalen, 1847, **64**, 332 ; Krafft and Stauffer, Ber. 1882, **15**, 1729), phosphorus oxychloride or pentachloride (Wallach, Annalen, 1877, **184**, 21 ; Corson, Scott, and Vose, Organic Syntheses, 1930, **10**, 66), or thionyl chloride (Michaelis and Sieber, Annalen, 1893, **274**, 312). Nitriles may also be obtained directly from carboxylic acids by distillation with potassium or lead thiocyanate (Letts, Ber. 1872, **5**, 669 ; Kekulé, *ibid.* 1873, **6**, 110 ; Krüss, *ibid.* 1884, **17**, 1767) or by heating with phospham :

$$2RCO_2H+N_2HP \rightarrow 2RCN+H_3PO_4$$

(G.P. 101391).

(vi) *Preparation of Esters.*—The direct esterification of a carboxylic acid with an alcohol,

$$RCO_2H + R'OH \rightleftharpoons RCO_2R' + H_2O,$$

is a reversible reaction and equilibrium is only set up slowly in the absence of a catalyst. The ease of esterification is largely dependent on the structure of the acid and of the alcohol (*cf. inter al.* Menschutkin, Annalen, 1879, **195**, 334; Ber. 1909, **42**, 4020; Willstätter *et al.*, Annalen, 1907, **354**, 249; 1910, **378**, 98; Michael *et al.*, Ber. 1909, **42**, 3157; 1910, **43**, 464; Sudborough *et al.*, J.C.S. 1908, **93**, 210; 1912, **101**, 237, 317, 1227); in general primary alcohols react more readily than secondary, and tertiary alcohols and phenols scarcely at all, while α substituents in carboxylic acids retard esterification; $\beta\gamma$-unsaturated acids are more readily esterified than their $\alpha\beta$-isomerides, a fact that has been employed in their separation (Eccott and Linstead, J.C.S. 1929, 2153).

The catalysts most commonly employed are sulphuric acid, when the mixture is usually heated on the water-bath (*cf.* Meyer, Monatsh. 1904, **23**, 840), and, generally better, a small amount of hydrogen chloride, when the reaction is usually carried out in the cold (Fischer and Speier, Ber. 1895, **28**, 3252; Adams and Chiles, Organic Syntheses, 1925, **5**, 53). When sulphuric acid is used as catalyst it is frequently advantageous to carry out the reaction with benzene as a diluent (Taylor, J.C.S. 1905, **87**, 1752). Other catalysts, such as metallic sulphates (Bogojawlenski and Narbutt, Ber. 1905, **38**, 3344; Clemmensen and Heitman, Amer. Chem. J. 1909, **42**, 319), phosphoric acid (Raikow and Tischkow, Chem. Ztg. 1905, **29**, 1268), phosphorus oxychloride (Nencki, J. pr. Chem 1882, [ii], **25**, 282), and Twitchell's reagent (Zaganiaris and Varvoglis, Ber. 1936, **69**, [B], 2277) have been proposed. For special cases a process has been used extensively which consists essentially of distillation in alcohol vapour with return of the distillate after de-hydration (Frankland and Aston, J.C.S. 1901, **79**, 517; Houssa Kenyon and Phillips, J.C.S. 1929, 1707; Kenyon, Organic Syntheses, 1925, **5**, 60; Corson, Adams and Scott, *ibid.* 1930, **10**, 48). Similar processes in which calcium carbide is used as the dehydrating agent (Thielepape, Ber. 1933, **66**, [B], 1454) and in which the water is removed as a ternary mixture with the alcohol and some third component (Clarke and Davis, Organic Syntheses, 1922, **2**, 23; Kendall and McKenzie, *ibid.* 1923, **3**, 51; McDermott, *ibid.* 1930, **10**, 88) have also been used. Special methods such as these have found application in the preparation of half-esters of dibasic acids (Contzen Crowet, Bull. Soc. chim. Belg. 1926, **35**, 165; Fourneau and Sabetay, Bull. Soc. chim. 1928, [iv], **43**, 859).

A procedure which finds wide application, especially for the preparation of very pure esters, is the reaction between the silver salt of the acid and an alkyl halide,

$$RCO_2Ag + R'X \rightarrow RCO_2R' + AgX,$$

which is best carried out by refluxing the components in ethereal solution (Hofmann and Cahours, Annalen, 1857, **102**, 294; Hesse, *ibid.* 1859, **110**, 340; Meyer and Jugilewitsch, Ber. 1897, **30**, 780); the sodium salt of the acid may be employed in the same way (*cf.* Reid, J. Amer. Chem. Soc. 1917, **39**, 107, 124). A somewhat analogous reaction is the preparation of methyl esters by treatment of an aqueous solution of the sodium salt with dimethyl sulphate (Werner and Seybold, Ber. 1904, **37**, 3658; von Liebig, *ibid.* 4036; Meyer, *ibid.* 4144; Gräbe, Annalen, 1905, **340**, 244).

In difficult cases, the action of diazomethane (for preparation, *see* Arndt, Organic Syntheses, 1935, **15**, 3) on the acid may be employed for the preparation of the methyl ester:

$$RCO_2H + CH_2N_2 \rightarrow RCO_2{\cdot}CH_3 + N_2;$$

this is generally carried out by treating the acid with an ethereal solution of diazomethane until the yellow colour of the latter is no longer discharged on standing (H. von Pechmann, Ber. 1895, **28**, 856; 1898, **31**, 501). The action of alcohols on acyl chlorides,

$$RCOCl + R'OH \rightarrow RCO_2R' + HCl,$$

is also sometimes of value in such cases (Baeyer, Annalen, 1888, **245**, 140). In the aromatic series acyl chlorides are condensed with phenols by shaking in the cold with a slight excess of caustic alkali (Schotten, Ber. 1884, **17**, 2545; Baumann, Ber. 1886, **19**, 3219) or, in the case of alkali-sensitive phenols, by heating on the water-bath with pyridine (Einhorn, Annalen, 1898, **301**, 95); it is occasionally advantageous to carry out the reaction in a neutral solvent, such as benzene, in the presence of powdered caustic alkali (Claisen, Ber. 1894, **27**, 3182).

Acid anhydrides also react with alcohols yielding esters (*cf.* Verley and Bolsing, Ber. 1901, **34**, 3354; Kaufmann, Ber. 1909, **42**, 3480); the reaction is most valuable in the case of dibasic acids, since their anhydrides react readily with sodium alkoxides to yield half-esters:

(Brühl, Ber. 1893, **26**, 284, 1097; Blaise and Kœhler, Bull. Soc. chim. 1910, [iv], **7**, 218; Auwers, Annalen, 1896, **292**, 178; Wegscheider and Hecht, Monatsh. 1903, **24**, 413; Anschütz, Annalen, 1907, **354**, 130).

Tertiary alcohols are only esterified with difficulty, if at all, by the above methods; their esters may be obtained by treatment of the alcohol with the Grignard reagent followed by addition of an acid chloride or anhydride to the resulting complex:

(1) $ROH + R'MgX \rightarrow ROMgX + R'H$

(2*a*) $ROMgX + R''COCl \rightarrow RO{\cdot}COR'' + MgXCl$

or (2*b*) $ROMgX + (R''CO)_2O \rightarrow RO{\cdot}COR'' + R''CO_2MgX$

(Houben, Ber. 1906, **39**, 1738; Henry, Bull. Acad. roy. Belg. 1907, 285; G.P. 162863). Tertiary esters may also be obtained by addition of fatty acids to olefins under the influence of

zinc chloride (Kondakow, J. pr. Chem. 1893, (ii), 48, 477).

(vii) *Preparation of Per-acids and Peroxides.*—Acyl peroxides are obtained by treatment of acyl chlorides with sodium peroxide or alkaline hydrogen peroxide :

$$2RCOCl+Na_2O_2 \rightarrow RCO{\cdot}O{\cdot}O{\cdot}COR+2NaCl$$

(H. von Pechmann and Vanino, Ber. 1894, 27, 1510 ; Vanino and Thiele, Ber. 1896, 29, 1726 ; Gambarjan, Ber. 1909, 42, 4008). Benzoyl peroxide is comparatively inert, but treatment with alcoholic sodium ethoxide yields the reactive perbenzoic acid, $PhCO{\cdot}O{\cdot}OH$, (Baeyer and Villiger, Ber. 1900, 33, 1576 ; Tiffeneau, Organic Syntheses, 1928, 8, 30 ; Braun, *ibid.* 1933, 13, 86), which is used very widely for oxidising ethylenic compounds.

Acetyl peroxide is obtained by the action of sodium peroxide on acetic anhydride in etherial solution (Nef, Annalen, 1897, 298, 288) or by the action of hydrogen peroxide on acetyl chloride (D'Ans and Friederich, Z. anorg. Chem. 1911, 73, 357). It is more reactive than benzoyl peroxide and is hydrolysed by water to peracetic acid (D'Ans and Frey, Ber. 11912, 45, 1848) which is also used for the oxidation of unsaturated compounds.

(viii) *Decarboxylation of Carboxylic Acids.*—In general monocarboxylic acids do not readily lose carbon dioxide on heating, but the introduction of negative substituents on the α-carbon atom greatly increases the tendency to undergo decarboxylation. Thus malonic acid and its substitution products readily lose carbon dioxide on heating, a reaction which is the basis of the malonic ester synthesis (*see above*). Certain other acids behave similarly ; thus nitroacetic acid is slowly decarboxylated at room temperature, yielding nitromethane (Steinkopf, Ber. 1909, 42, 3925) and phenylacetic acid gives a good yield of toluene on prolonged heating at 350°–375° (Engler and Löw, Ber. 1893, 16, 1436); the thermal decarboxylation of cinnamic acid.

$$PhCH{:}CH{\cdot}CO_2H \rightarrow PhCH{:}CH_2+CO_2,$$

is used for the preparation of styrene, the process consisting merely of slow distillation in the presence of a little hydroquinone to prevent polymerisation of the hydrocarbon (Abbott and Johnson, Organic Syntheses, 1928, 8, 85). The reaction frequently proceeds readily in aqueous solution and is the basis of Kolbe's method of preparing nitromethane, in which sodium chloroacetate is treated with sodium nitrite and the resulting nitroacetic acid decarboxylated directly by heating the solution (Kolbe, J. pr. Chem. 1872, [ii], 5, 427 ; Whitmore and Whitmore, Organic Syntheses, 1923, 3, 83) ; the method may be applied to higher homologues using the appropriate α-chloroacids (Auger, Bull. Soc. chim. 1900, [iii], 23, 333). An analogous reaction is the preparation of ω-bromostyrene by simultaneous elimination of hydrogen bromide and carbon dioxide from dibromo cinnamic acid by heating with water or aqueous alkali :

$$PhCHBr{\cdot}CHBr{\cdot}CO_2H \rightarrow PhCH{:}CHBr+HBr+CO_2$$

(Fittig and Binder, Annalen, 1879, 195, 141 ; Nef, *ibid.* 1899, 308, 267). 2:4:6-Trinitrobenzoic acid is readily decarboxylated by heating in aqueous solution, the reaction affording a convenient method of preparation of *sym*-trinitrobenzene (Clarke and Hartman, Organic Syntheses, 1922, 2, 93). Decarboxylation may in some cases be brought about by heating with bases such as pyridine or aniline (Staudinger, Ber. 1906, 39, 3067).

(ix) *Preparation of Aldehydes and Ketones from Carboxylic Acids.*—It was early discovered that dry distillation of the calcium or barium salts of fatty acids led to the production of ketones :

$$\begin{matrix}RCO_2\diagdown \\ \qquad Ca \\ RCO_2\diagup\end{matrix} \rightarrow \begin{matrix}R\diagdown \\ \qquad CO \\ R\diagup\end{matrix} + CaCO_3$$

(Liebig, Annalen, 1832, 1, 225). Mixed ketones may be prepared by using a mixture of salts, and distillation of the barium salt of a fatty acid with barium formate yields aldehydes :

$$(R{\cdot}CO_2)_2Ba+(H{\cdot}CO_2)_2Ba \rightarrow 2R{\cdot}CHO+2BaCO_3$$

Although the yields are generally poor the method has found application in special cases (Morgan and Holmes, J.S.C.I. 1925, 44, 108T, 491T ; Tiemann, Ber. 1898, 31, 826 ; Davies, Heilbron, Jones, and Lowe, J.C.S. 1935, 584).

In the case of dibasic acids, cyclic ketones are obtained, *e.g.*, adipin ketone from barium adipate :—

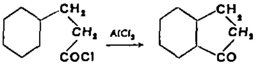
$$\begin{matrix}CH_2{\cdot}CH_2{\cdot}CO_2\diagdown \\ | \qquad\qquad\quad Ba \\ CH_2{\cdot}CH_2{\cdot}CO_2\diagup\end{matrix} \rightarrow \begin{matrix}CH_2{\cdot}CH_2\diagdown \\ | \qquad\quad CO \\ CH_2{\cdot}CH_2\diagup\end{matrix} + BaCO_3$$

(Hentzschel and Wislicenus, Annalen, 1893, 275, 312 ; Wislicenus, *ibid.* 341, 351, 356). In general, only a small " catalytic " amount of baryta is added to the dibasic acid, dry distillation then giving a good yield of ketone (Thorpe and Kon, Organic Syntheses, 1925, 5, 37 ; Linstead and Meade, J.C.S. 1934, 942) ; stereoisomeric dibasic acids generally require heating to different temperatures to bring about ketonisation, stereoisomeric ketones often being formed (*cf.* Zelinsky, Ber. 1896, 29, 1541 ; Zelinsky and Rudsky, Ber. 1897, 30, 404 ; Faltis and Wagner, Annalen, 1923, 433, 103 ; Barrett and Linstead, J.C.S. 1935, 441). Variants of the method consist in heating the acid with iron filings or heavy metal salts (G.P. 256622), and slow distillation of the acid with carbon dioxide (Aschan, Ber. 1912, 45, 1605). General studies of the efficacy of various metallic compounds as catalysts have been carried out (Ruzicka *et al.*, Helv. Chim. Acta, 1926, 9, 249, 399, 499 ; 1928, 11, 496, 670, 686 ; 1930, 13, 1152 ; Vogel, J.C.S. 1928, 2032) ; in general distillation of the thorium, cerium or yttrium salts gives very good results.

A further method consists in distilling the acid with acetic anhydride (Blanc, Compt. rend. 1907, 144, 1356 ; Bull. Soc. chim. 1908, [iv], 3, 778, 780). It is generally assumed that acids of the succinic and glutaric series give an-

hydrides and acids of the adipic and pimelic series, ketones, by this method—the so-called "*Blanc rule*"; *this, however, does not always* hold and should be employed with caution. Rearrangement also sometimes accompanies ketonisation (Ruzicka and Brugger, Helv. Chim. Acta, 1926, 9, 399; Day, Kon and Stephenson, J.C.S. 1920, **117**, 642; Nef, Annalen, 1900, **310**, 333).

A good method for aliphatic ketones is the passage of a fatty acid or a mixture of fatty acids through a tube containing thoria heated to 400° (Senderens, Compt. rend. 1909, **148**, 927, *149*, *213*, *905*; *Pickard and Kenyon*, J.C.S 1911, **99**, 56; 1912, **101**, 628; 1913, **103**, 1936; Herbert and Manske, Organic Syntheses, 1936, **16**, 47). A method applicable to semi-aromatic ketones is the Friedel Crafts auto-condensation of aromatic acyl chlorides:



(Kipping, J.C.S. 1894, **65**, 480; Martin and Fieser, Organic Syntheses, 1935, **15**, 77).

(x) *Reduction of Carboxylic Acids and Derivatives.*—In general, free carboxylic acids are reduced to aldehydes or primary alcohols only with difficulty. Under appropriate conditions, however, aromatic *o* hydroxy-carboxylic acids can be reduced to aldehydes and finally to alcohols by means of sodium amalgam (R. von den Velden, J. pr. Chem. 1877, [ii], **15**, 163; Weil *et al.*, Ber. 1908, **41**, 4147; 1921, **54**, 3217; 1922, **55**, 224, 301, 2664). Aromatic acids have been successfully reduced to aldehydes electrolytically (Tafel and Friedrichs, Ber. 1904, **37**, 3187; Mettler, Ber. 1905, **38**, 1745; 1906, **39**, 2933; Marie, Marquis, and Birckenstock, Bull. Soc. chim. 1919, [iv], **25**, 512). Aldehydes are also formed when a mixture of the acid vapour with formic acid vapour is passed over titanium dioxide at 250°–300° (Sabatier and Mailhe, Compt. rend. 1912, **154**, 561).

A method for the reduction of acyl chlorides to aldehydes which has found wide application is that developed by Rosenmund and his co-workers (Ber. 1918, **51**, 585; 1921, **54**, [B], 425, 638, 2038, 2888; 1922, **55**, [B], 2360; 1923, **56**, [B], 1481); the method is essentially a catalytic hydrogenation in the presence of palladised barium sulphate or kieselguhr in boiling xylene or cumene, a "regulator," such as quinoline which has previously been heated with sulphur, being present to prevent the reduction going further.

The imino-chlorides (see below) derived from anilides form the basis of the following method of reduction:

$$PhCO_2H \rightarrow PhCO\,NHPh \rightarrow PhCCl{:}NPh$$
$$\downarrow$$
$$Ph{\cdot}CHO + NH_2Ph \leftarrow PhCH{:}NPh$$

(Sonn and Müller, Ber. 1919, **52**, 1927), which is based on the reduction of the imino-chloride with stannous chloride, yielding an azomethine which is readily hydrolysed to an aldehyde and aniline. Another, somewhat similar, method is based on the following series of reactions:

$$RCCl{:}NPh \rightarrow RC\begin{matrix}\nearrow NPh\\ \searrow MgCl\end{matrix}$$
$$\rightarrow RCH{:}NPh \rightarrow RCHO + PhNH_2$$

(Staudinger, Ber. 1908, **41**, 2217).

A method of very wide application is the reduction of esters with sodium and alcohol (Bouveault and Blanc, Compt. rend. 1903, **136**, 1676; **137**, 60; Bull. Soc. chim. 1904, [iii], *31*, *669*; *cf. Ford and Marvel, Organic* Syntheses, 1930, **10**, 62); the yields are somewhat variable and a number of modifications have been described, but, generally, an alcoholic solution of the ester is run on to a large excess of clean sodium in a capacious flask; when the initial reaction is finished the product is refluxed in an oil-bath until all the sodium is dissolved —prolongation of this heating improves the yield (Rydon, J.C.S. 1936, 594); the process of working up depends on the properties of the product. Butyl and amyl alcohols have been used in order to increase the maximum temperature (Reid, Cockerille, Meyer, Cox and Ruhoff, Organic Syntheses; 1935, **15**, 51). This method of reduction has also been applied to the anhydrides of dibasic acids, lactones being formed (Blanc, Bull. Soc. chim. 1905, [iii], **33**, 898), while the reduction of dibasic esters to glycols has been fully worked out (Bennett and Mosses, J.C.S. 1931, 1697, Manske, Organic Syntheses, 1934, **14**, 20). Sodium in acid aqueous sodium acetate has also been employed for the reduction of esters (Prins, Rec. trav. chim. 1923, **42**, 1050) and Bouveault and Blanc's method modified by carrying out the reduction using sodium and butyl alcohol in a hydrocarbon solvent (Ford and Marvel, Organic Syntheses, 1930, **10**, 62; Levene and Allen, J. Biol. Chem. 1916, **27**, 443; Bleyberg and Ulrich, Ber. 1931, **64**, [B], 2504).

Amides on reduction by the Bouveault-Blanc procedure give mixtures of amines and alcohols (Guerbet, J. Pharm. Chim. 1899, [vi], *10*, *180*; *Bouveault and Blanc, Compt. rend.* 1904, **138**, 148). Catalytic hydrogenation of esters to alcohols using copper chromite (Adkins and Folkers, J. Amer. Chem. Soc. 1931, **53**, 1095; 1932, **54**, 1145) and other catalysts (Schrauth, Schenck, and Stickdorn, Ber. 1931, **64**, 1314; Schmidt, *ibid.* 2051) has also been employed.

(xi) *Bromination of Fatty Acids.*—Bromination and chlorination of saturated carboxylic acids occur in the *a*-position and the reaction is of great importance for synthetic operations. Acyl halides are brominated more readily than the acids themselves and are employed in preference; it is usually unnecessary to isolate the free halide, red phosphorus and bromine in the right proportions being allowed to react directly with the acid (Volhard, Annalen, 1887, **242**, 141; Zelinsky, Ber. 1887, **20**, 2026; Hell *et al.*, Ber. 1889, **22**, 1745; 1891, **24**, 938, 2390; Le Sueur, J.C.S. 1905, **87**, 1895). The quantity of phosphorus used may be considerably less than the theoretical (Lapworth,

J.C.S. 1904, **85**, 41 ; Ward, J.C.S. 1922, **121**, 1161) or a small amount of phosphorus trichloride may be used (Clarke and Taylor, Organic Syntheses, 1925, **4**, 9). It is generally, however, cleaner to convert the acid into the acyl chloride with thionyl chloride and then to brominate this without purification. It is sometimes convenient to brominate malonic acids, without solvent or catalyst, and then to decarboxylate the product (*cf.* Marvel and Du Vigneaud, Organic Syntheses, 1931, **11**, 20) ; malonic esters can also be brominated directly in solvents such as carbon tetrachloride (Palmer and McWherter, Organic Syntheses, 1927, **7**, 34).

(xii) *Degradation of Fatty Acids.*—An important reaction of carboxylic acids is their conversion to amines by the Hofmann degradation, whereby the amide is treated with bromine and alkali :

$$RCO{\cdot}NH_2+Br_2+KOH \rightarrow RCO{\cdot}NHBr+KBr+H_2O$$

$$RCO{\cdot}NHBr+3KOH \rightarrow RNH_2+KBr+K_2CO_3+H_2O$$

(Hofmann, Ber. 1882, **15**, 752 ; 1884, **17**, 1406). The reaction is of importance for descending a homologous series (*cf.* Hoogewerff and van Dorp, Rec. trav. chim. 1888, **6**, 373 ; 1891, **10**, 4 ; Moore, Marrack and Proud, J.C.S. 1921, **119**, 1786 ; Beckmann and Correns, Ber. 1922, **55**, 850).

An analogous procedure is that of Curtius (J. pr. Chem. 1894, [ii], **50**, 275 ; 1901, [ii], **64**, 297, 401, 419) wherein the hydrazide is converted into the azide with nitrous acid :

$$RCO{\cdot}NH{\cdot}NH_2+HNO_2 \rightarrow RCO{\cdot}N_3+2H_2O$$

The azide is then boiled with alcohol, when it is converted to the urethane :

$$RCO{\cdot}N_3+EtOH \rightarrow RNH{\cdot}CO_2Et+N_2$$

which is then readily hydrolysed to the amine :

$$RNH{\cdot}CO_2Et+H_2O \rightarrow RNH_2+CO_2+EtOH$$

Another valuable method consists in treatment of the acid with hydrazoic acid, the amine being formed directly :

$$RCO_2H+N_3H \rightarrow RNH_2+N_2+CO_2$$

(B.P. 307789 ; J. von Braun, Annalen, 1931, **490**, 125 ; *cf.* Jenson and Pope, Proc. Roy. Soc. 1936, **154**, A, 54). A further method (Le Sueur, J.C.S. 1905, **87**, 1888) is based on the following series of reactions :

$$RCH_2{\cdot}CO_2H \rightarrow RCHBr{\cdot}CO_2H \rightarrow RCH(OH){\cdot}CO_2H \rightarrow R{\cdot}CHO$$

(xiii) *Chain-Lengthening in Carboxylic Acids.*—The most obvious process for chain lengthening is based on the transformations :

$$\begin{array}{l} RCO_2H \rightarrow RCO_2Et \rightarrow RCH_2{\cdot}OH \rightarrow RCH_2X \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad RCH_2{\cdot}CO_2H \leftarrow RCH_2{\cdot}CN \end{array}$$

(*cf.* Blanc, Bull. Soc. chim. 1908, [iv], **3**, 291). This process may also be brought about very smoothly by converting the acid chloride to the corresponding diazo-ketone by treatment with diazomethane :

$$RCOCl+2CH_2N_2 \rightarrow RCO{\cdot}CHN_2+CH_3Cl+N_2$$

The diazoketone may then undergo rearrangement, under a variety of experimental conditions, with loss of nitrogen, yielding the higher homologue of the carboxylic acid :

$$RCO{\cdot}CHN_2+H_2O \rightarrow RCH_2{\cdot}CO_2H+N_2$$

(Arndt and Eistert, Ber. 1935, **68**, [B], 200; 1936, **69**, [B], 1805).

Reactions of Carboxylic Acid Derivatives.—(i) *Amides, Imides, Etc.*—Amides may be hydrolysed by refluxing with aqueous or alcoholic alkali until the evolution of ammonia is complete ; hot mineral acids also bring about the hydrolysis of amides and are to be preferred in the case of anilides and other substituted amides. In difficult cases, amides may be converted into carboxylic acids by means of nitrous acid (Bouveault, Bull. Soc. chim. 1892, [iii], **9**, 368) ; this procedure is only applicable to unsubstituted amides, those with one substituent on the nitrogen, such as anilides, alkylureas, and urethanes, forming nitroso-derivatives :

$$RCO{\cdot}NHR'+HNO_2 \rightarrow RCO{\cdot}NR'{\cdot}NO+H_2O$$

This last reaction is best brought about by the action of nitrous fumes in acetic acid solution (Fischer, Ber. 1876, **9**, 463 ; H. von Pechmann, Ber. 1895, **28**, 856 ; Hantzsch and Wechsler, Annalen, 1902, **325**, 237 ; Jacobson and Huber, Ber. 1908, **41**, 663), but may also be carried out using aqueous nitrous acid, this method being particularly useful with alkylureas (Werner, J.C.S. 1919, **115**, 1096).

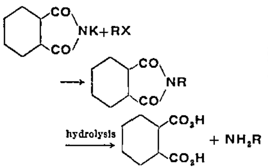
Amides may be reduced, catalytically, to amines :

$$RCO{\cdot}NH_2 \rightarrow RCH_2{\cdot}NH_2$$

(Adkins and Wojcik, J. Amer. Chem. Soc. 1934, **56**, 247, 2419) thus affording a further method for chain-lengthening.

Amides react with hypohalogenites to yield halogeno-amides of the type $RCO{\cdot}NXR'$ (Mauquin, Ann. Chim. 1911, [viii], **22**, 305 ; Pyman, J.C.S. 1913, **103**, 857) ; the halogen in these compounds is very labile and they may be used as mild halogenating agents, a notable example being the rearrangement of *N*-chloroacetanilide to *p*-chloroacetanilide, a process which may be regarded as one of auto-substitution (Chattaway and Orton, J.C.S. 1899, **75**, 1046 ; 1900, **77**, 789, 797, 800 ; 1901, **79**, 274). The bromoamides are the basis of the Hofmann method of degradation, to which reference has already been made ; if the decomposition of the bromoamides is carried out in the presence of unchanged amide, acyl alkyl ureas are produced (Hofmann, Ber. 1881, **14**, 2725 ; 1882, **15**, 752 ; Odenwald, Annalen, 1918, **416**, 228), while treatment of the bromoamide with alcoholic alkoxides yields urethanes (Jeffreys, Ber., 1897, **30**, 898 ; Gutt, Ber. 1907, **40**, 2062).

Anilides react with phosphorus pentachloride to form imino chlorides of the type R·CCl:NPh (Wallach, Annalen, 1877, **184**, 5; Sonn and Müller, Ber. 1919, **52**, 1930). Although not markedly basic, amides form salts with halogen acids (Werner, Ber. 1903, **36**, 153; Dadswell and Kenner, J.C.S. 1927, 1104). Metallic derivatives of the type RCO NHNa are known (Titherley, J.C.S. 1897, **71**, 467; Strecker), Annalen, 1857, **103**, 324), the alkali derivatives of certain imides, e g. potassium phthalimide, being produced very readily from the imide and alcoholic potassium hydroxide (Hale and Britton, J. Amer. Chem. Soc. 1919, **41**, 843). Treatment of these derivatives with alkyl halides brings about *N*-alkylation (Hepp, Ber. 1877, **10**, 328; Pictet and Crépieux, Ber. 1888, **21**, 1107); if the silver salts are used O-alkyl derivatives of the enol are formed in addition (Wheeler and Johnson, Amer. Chem. J. 1899, **21**, 185; 1900, **23**, 136; Lander, J C.S. 1903, **83**, 415, 766). The alkylation of alkali metal derivatives of imides is the basis of Gabriel's well-known method for introducing amino-groups:



(Gabriel *et al.*, Ber. 1887, **20**, 2224, 2869; 1888, **21**, 566, 2669; 1889, **22**, 1771; 1892, **25**, 3056, 1893, **26**, 2197; 1902, **35**, 3805; Osterberg, Organic Syntheses, 1927, **7**, 78).

With the Grignard reagent amides yield ketones (Béis, Compt. rend. 1903, **137**, 575; McKenzie and Wren, J.C S. 1908, **93**, 310; Wren, J.C.S. 1909, **95**, 1583).

(ii) *Acyl Halides.*—Aliphatic acyl chlorides are very readily hydrolysed to the acids when brought into contact with water, the reaction sometimes proceeding with almost explosive violence; in the aromatic series the reaction is much slower and frequently refluxing with caustic alkali is necessary to bring about complete hydrolysis; the analogous reaction with alcohols, yielding esters, has already been discussed.

Acyl chlorides may be converted into the bromides or iodides by saturation with the appropriate hydrogen halide, followed by distillation (Staudinger and Anthes, Ber. 1913, **46**, 1417; Gustus and Stevens, J. Amer. Chem. Soc. 1933, **55**, 374). Acyl fluorides may be obtained by treatment of the chlorides with silver fluoride (Guenez, Bull. Soc. chim. 1886, [iii], **5**, 887; Meslans, Ann. Chim. 1894, [vii], **1**, 405) or with zinc fluoride (Meslans and Girardet, Bull. Soc. chim. 1896, [iii], **15**, 878; Borodin, Compt. rend. 1863, **55**, 555).

Acyl cyanides, *i.e.* α-keto-nitriles, R CO CN, are obtained by heating acyl chlorides with silver cyanide (Hubner, Annalen, 1861, **120**, 334; Claisen *et al.*, Ber. 1878, **11**, 1565; 1880, **13**, 2121) or, better, by treatment of the acyl chloride with hydrogen cyanide and pyridine in an inert solvent (Claisen, Ber. 1898, **31**, 1023; Mauthner, Ber. 1909, **42**, 188). With silver nitrate, acyl nitrates are obtained (Francis, J.C.S. 1906, **89**, 1; Ber. 1906, **39**, 3798).

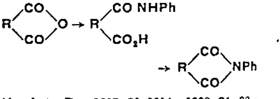
With diazomethane in ethereal solution acyl chlorides yield diazoketones (Arndt and Amende, Ber. 1928, **61**, 1122; Bradley and Robinson, *J.C.S. 1928, 1310; Bradley, Robinson,* and Schwarzenbach, J.C.S. 1930, 797), a reaction which is the basis of Arndt's synthetic process (*see above*).

The reaction of acyl chlorides with zinc alkyl halides is a very important method of preparing ketones:

$$\mathrm{RCOCl + R'ZnX \rightarrow RCOR' + ZnXCl}$$

It is carried out in a hydrocarbon solvent, usually toluene or petroleum, using ethyl acetate as a catalyst (Blaise, Bull. Soc. chim. 1911, [iv], **9**, 1; Wohlgemuth, Compt. rend. 1914, **159**, 80). With the Grignard reagent, tertiary alcohols are the final product, but it is possible to stop the reaction at the ketone stage (Acree, Ber. 1904, **37**, 628; Oddo, Ber. 1910, **43**, 1012).

(iii) *Anhydrides.*—Anhydrides are, in general, hydrolysed much more slowly than are acyl halides. The cyclic anhydrides of dibasic acids are best characterised by treatment with aniline in benzene solution; the mono-anilides so formed are converted into anils on heating:



(Anschutz, Ber. 1887, **20**, 3214; 1888, **21**, 88; Annalen, 1890, **259**, 137; Auwers, *ibid.* 1895, **285**, 227). With 1 molecular proportion of the Grignard reagent, anhydrides yield ketones (Fournier, Bull. Soc. chim. 1910, [iv], **7**, 836).

(iv) *Esters.*—Esters are usually hydrolysed to acids by refluxing with caustic alkali either in aqueous or in alcoholic solution; this process may be applied to their quantitative determination. It is occasionally more convenient to carry out hydrolysis by refluxing with dilute mineral acids; certain esters, such as those of α-hydroxy and α-amino-acids, are hydrolysed by standing or boiling with water alone (Schreiner, Annalen, 1879, **197**, 7; Findlay *et al.*, J.C.S. 1909, **95**, 1004; 1905, **87**, 747; Fischer, Ber. 1901, **34**, 445). Regulation of the amount of caustic alkali used for hydrolysis enables polycarboxylic esters to be hydrolysed to partial esters (Freund, *Ber. 1884, 17, 780;* Marguery, Bull. Soc. chim. 1905, [iii], **33**, 543).

An analogous reaction is alcoholysis:

$$\mathrm{RCO_2R' + R''OH \rightleftharpoons RCO_2R'' + R'OH}$$

It may be brought about by heating the alcohol-ester mixture in sealed tubes (Friedel and Crafts, Annalen, 1864, **130**, 198; 1865, **133**, 207; Grün,

Ber. 1921, **54**, 294) or by using sodium alkoxides as catalysts (Bouis, J. pr. Chem. 1857, [i], **72**, 308 ; Claisen, Ber. 1887, **20**, 646 ; Purdie *et al.*, J.C.S. 1888, **53**, 391; ; 1885, **47**, 855 ; 1887, **51**, 627 ; Reimer and Downer, J. Amer. Chem. Soc. 1921, **43**, 945 ; Bainbridge, J.C.S. 1914, **105**, 2297 ; Zemplén and Pacsu, Ber. 1929, **62**, [B], 1613) ; potassium carbonate is also effective as a catalyst (Fischer, Ber. 1920, **53**, [B], 1634).

The condensation of esters with one another has already been discussed ; esters react similarly with methyl ketones, 1:3-diketones being formed :

$$RCO_2Et + CH_3{\cdot}COR' \rightarrow RCO{\cdot}CH_2{\cdot}COR' + EtOH$$

This reaction is generally brought about with metallic sodium (Claisen, Annalen, 1893, **277**, 168 ; Morgan *et al.*, J.C.S. 1923, **123**, 447 ; 1924, **125**, 740, 756, 760, 1271 ; 1925, **127**, 2620), but sodamide may also be used successfully (Claisen, Ber. 1905, **38**, 694). Ketones of the type $RCO{\cdot}CH_2R'$ give only poor yields (Morgan, Drew, and Porter, Ber. 1925, **58**, 336).

With the Grignard reagent esters yield tertiary alcohols :

$$RCO_2Et \xrightarrow{R'MgX} RCR'_2{\cdot}OH$$

(Grignard, Compt. rend. 1900, **130**, 1322) a reaction that has found very extensive application (*cf.* Perkin, J.C.S. 1904, **85**, 654) ; if the resulting alcohol is readily dehydrated this often occurs during the reaction and the corresponding unsaturated hydrocarbon is isolated (*cf.* Kay and Perkin, J.C.S. 1906, **89**, 839). Dibasic esters normally yield di-tertiary glycols (Valeur, Compt. rend. 1901, **132**, 833 ; Bull. Soc. chim. 1903, [iii], **29**, 683 ; Dilthey and Last, Ber. 1904, **37**, 3640), but, by suitable modification of the conditions, the attack of the reagent may be confined to only one of the ester groups, yielding a hydroxy-ester (Hepworth, J.C.S. 1919, **115**, 1203). When *αβ*-unsaturated esters are used the reaction may be complicated by addition of the reagent to the double bond (Kohler and Heritage, Amer. Chem. J. 1905, **34**, 132 ; 1905, **33**, 21, 153).

(v) *Nitriles.*—On treatment with alcoholic sulphuric or hydrochloric acid in the presence of a little water, nitriles yield esters :

$$RCN + R'OH + H_2O \rightarrow RCO_2R' + NH_3$$

(Beckurts and Otto, Ber. 1876, **9**. 1590 ; Pfeiffer and Matton, Ber. 1911, **44**, 1115; Spiegel, Ber. 1918, **51**, 296 ; Adams and Thal, Organic Syntheses, 1922, **2**, 27 ; Nelson and Cretcher, J. Amer. Chem. Soc. 1928, **50**, 2758).

Nitriles are readily reduced to primary amines by sodium and alcohol :

$$RCN + 2H_2 \rightarrow RCH_2{\cdot}NH_2$$

(Ladenburg, Ber. 1885, **18**, 2956 ; 1886, **19**, 780 ; Wohl and Berthold, Ber. 1910, **43**, 2183 ; Suter and Moffett, J. Amer. Chem. Soc. 1934, **56**, 48). Catalytic hydrogenation by the Sabatier-Senderens method (Compt. rend. 1905, **140**, 482) or with platinum or palladium in alcoholic solution (Paal and Gerum, Ber. 1909, **42**, 1553) gives rise to considerable amounts of secondary amines ; primary amines are, however, the sole product if hydrogenation is carried out in acetic acid solution (Rosenmund and Pfankuch, Ber. 1923, **56**, [B], 2258).

In dry alcoholic solution nitriles react with hydrogen chloride, forming imino-ether hydrochlorides :

$$RCN + EtOH + HCl \rightarrow RC\begin{matrix}\nearrow NH,HCl \\ \searrow OEt\end{matrix}$$

(Pinner, Ber. 1883, **16**, 352, 1643 ; 1890, **23**, 2917 ; Dox, Organic Syntheses, 1928, **8**, 1). Nitriles may be converted into aldehydes by the following series of reactions :

$$RCN \xrightarrow{HCl} RCCl{:}NH \xrightarrow{H_2} RCH{:}NH \xrightarrow{H_2O} RCHO + NH_3$$

which is usually carried out by adding the nitrile to stannous chloride suspended in ether saturated with dry hydrogen chloride (Stephen, J.C.S. 1925, **127**, 1874). Under the influence of hydrogen chloride and zinc chloride, nitriles condense with phenols, forming imines which are readily hydrolysed to hydroxy-ketones :

$$(OH)_2C_6H_4 + RCN + HCl \rightarrow (OH)_2C_6H_3{\cdot}CR{:}NH,HCl \rightarrow (OH)_2C_6H_3{\cdot}CO{\cdot}R + NH_4Cl$$

(Hoesch *et al.*, Ber. 1915, **48**, 1122 ; 1917, **50**, 462 ; Stephen, J.C.S. 1920, **117**, 1529).

With the Grignard reagent the first product is the ketimine :

$$RCN + R'MgX \rightarrow RR'C{:}NMgX \xrightarrow{H_2O} RR'C{:}NH + Mg(OH)X$$

which may be isolated if the complex is decomposed with ammonium chloride (Moureu and Mignonac, Compt. rend. 1913, **156**, 1801). Decomposition with dilute acid yields ketones :

$$RR'C{:}NMgX + 2HCl + H_2O \rightarrow RR'CO + MgX_2 + NH_4Cl$$

(Blaise, Compt. rend. 1901, **132**, 38 ; **133**, 299) and it is for this purpose that the reaction is generally employed (Shriner and Turner, J. Amer. Chem. Soc. 1930, **52**, 1268 ; Pratt and Robinson, J.C.S. 1923, **123**, 748).

Some nitriles yield amides with hydrogen peroxide (Radziszewski, Ber. 1885, **18**, 355) ; the method is occasionally convenient for preparative purposes (Noller, Organic Syntheses, 1933, **13**, 94).

Analysis.—(i) *Quantitative.*—The equivalent of a carboxylic acid is most easily determined by titration against $N/10$ barium hydroxide, using phenolphthalein as indicator. Occasionally it is more convenient to ignite the silver salt and weigh the bead of metallic silver so formed ; the analysis of other inorganic salts is also sometimes employed for this purpose.

(ii) *Qualitative.*—Carboxylic acids are best recognised by liberation of carbon dioxide from aqueous sodium or ammonium bicarbonate ; certain acids are also recognised by characteristic calcium, copper, lead, or ferric iron salts.

The methyl ester, amide, or imide are sometimes of value for characterisation; their preparation has already been discussed.

For purposes of identification anilides and *p*-toluidides of monobasic acids are obtained by refluxing the acid with 2 vols. of thionyl chloride for 30 minutes and then removing the excess of thionyl chloride under reduced pressure; the residue of acid chloride is taken up in dry ether and the theoretical amount of the base (aniline or *p* toluidine) is added cautiously in ethereal solution. The product is washed with dilute hydrochloric acid, when evaporation of the ether leaves the derivative, which is usually best crystallised from water, dilute alcohol, or benzene-petroleum. In the case of dibasic acids of the succinic or glutaric series, the anhydride is first prepared by refluxing the acid with an excess of acetyl chloride for 30 minutes; the excess of acetyl chloride is removed *in vacuo* and the residual anhydride is taken up in benzene and treated with a slight excess of aniline in the same solvent. The anilic acid usually crystallises out and may be crystallised from dilute alcohol Alternatively the acid is refluxed with an excess of aniline for 30 minutes and the resulting dianilide crystallised, usually from alcohol.

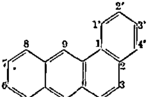
p-Bromophenacyl esters are extensively used for the characterisation of carboxylic acids (Judefind and Reid, J. Amer. Chem Soc. 1920, 42, 1044). The acid is not quite neutralised with aqueous sodium carbonate and one equivalent of a 10% alcoholic solution of *p*-bromophenacyl bromide is added. The product is refluxed for 30 minutes (longer for polybasic acids); on cooling or diluting with water, the *p*-bromophenacyl ester separates and may usually be recrystallised from dilute alcohol.

Phenacyl (Rather and Reid, J. Amer. Chem. Soc. 1919, 41, 75) and *p* phenylphenacyl (Drake and Bronitsky, J. Amer. Chem. Soc. 1930, 52, 3718; Wrede and Rothhaas, Ber. 1934, 67, 739) esters have also found wide application. Benzylamine and *a*-phenylethylamine salts have also been recommended (Buehler, Carson, and Edds, J. Amer. Chem. Soc. 1935, 57, 2181) as have the *p*-phenylanilides, which are most easily obtained by heating the acid with *p* xenylamine (Kimura and Nikayashi, Ber. 1935, 68, [B], 2028).

Carboxylic esters may be readily characterised by conversion into the corresponding anilides by treatment with anilinomagnesium bromide, which is easily obtained from aniline and ethyl magnesium bromide (Hardy, J.C.S. 1936, 398). H. N. R.

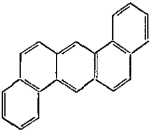
CARBROMAL, CARBROMALUM *v.* ADALINE.

CARCINOGENIC HYDROCARBONS. The experimental production of cancer was first achieved by Yamagiwa and Ichikawa (1915) by the application of coal tar to the ear of a rabbit, and later Tsutsui (1918) obtained malignant tumours by applying coal tar to the skin of the back of a mouse. Workers with coal tar, mineral lubricating oils, and shale oil are susceptible to skin cancer, and it appears that the cancer-producing action of coal tar and similar substances is due to certain constituents of the tar products. Kennaway (J. Path. Bact. 1924, 27, 233) showed that tars formed from isoprene and acetylene at high temperature in an atmosphere of hydrogen give strongly carcinogenic fractions and also that carcinogenic products are obtained by the action of aluminium chloride on (*a*) acetylene, (*b*) xylene, (*c*) naphthalene, (*d*) naphthalene and brombenzene, and (*e*) tetrahydronaphthalene. Of these (*d*) and (*e*) gave the most active materials (Biochem. J. 1930, 24, 497). Mayneord (1927) found that carcinogenic tars are characterised by the possession of three bands in their fluorescent spectra (at 4,000, 4,180, and 4,400Å), and it was then noted by Hieger (Biochem. J. 1930, 24, 505) that 1:2-benzanthracene (I)



I.

gives the characteristic three-banded fluorescent spectrum, the spectrum being shifted, however, towards the ultraviolet. Kennaway showed that 1.2 5 6-dibenzanthracene (II) when applied in benzene solution to the skin of mice gives rise to malignant tumours.

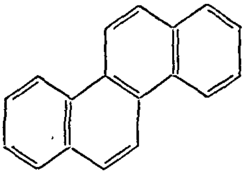


II.

The carcinogenic properties of 1.2 5 6-dibenzanthracene, 5 6 *cyclo*-penteno-1.2 benzanthracene and closely related compounds have been described by Cook, Hieger, Kennaway and Mayneord (Proc. Roy. Soc. B. 1932, 111, 455), Cook (*ibid.* 485), Burrows, Hieger and Kennaway (Amer. J. Cancer, 1932, 16, 57), Burrows (*ibid.* 1933, 17, 1); Barry and Cook (*ibid.* 1934, 20, 58). A systematic examination of the carcinogenic activities of tetracyclic and pentacyclic aromatic hydrocarbons is described in an article by Barry, Cook, Haslewood, Hewett, Hieger and Kennaway (Proc. Roy. Soc. B 1935, 117, 318). The technique by Barry *et al.* (*ibid.*) for the production of skin cancer consisted in applying the substance in solution to the interscapular region of mice twice weekly. Usually the compound was applied in benzene solution (0 3 g. in 100 ml.). Tests for the production of sarcoma were made by injecting the compound *sub cutem* in a fatty medium, such as lard.

Out of the possible six hydrocarbons containing four condensed benzene rings, 1:2-benz-

anthracene (I), and chrysene (III), are practically without activity.



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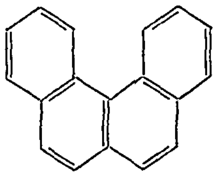
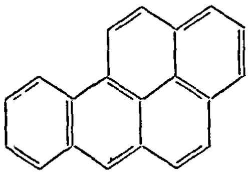


IV.

3:4-benzphenanthrene (IV) gave 12 tumours in a series of 20 mice, and it is the simplest hydrocarbon yet shown to have carcinogenic activity.

Out of the 15 possible hydrocarbons containing 5 condensed benzene rings, 12 have been examined, and only 2 (1:2:5:6-dibenzanthracene (II) and 3:4-benzpyrene (V) have been found to have pronounced activity.

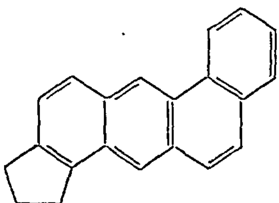


V.

Carcinogenic properties in the homologues of 1:2-benzanthracene are usually shown by compounds having substituents at positions 5 or 6 (*see* I), position 5 being more favourable, but rarely by compounds with substituents in other positions. The following tables, I and II, taken from an article by Cook (Chem. Weekblad, 1935, 32, 563), show the carcinogenic activities of various homologues of 1:2-benzanthracene and a list of non-carcinogenic homologues of this substance.

TABLE I.

Compound.	No. of mice.	Tumours formed.
1:2-benzanthracene	86	1
4-Me-1:2-benzanthracene . .	10	1
5-Me-1:2-benzanthracene . .	10	7
6-Me-1:2-benzanthracene . .	10	3
5:6-diMe-1:2-benzanthracene .	20	16
6:7-diMe-1:2-benzanthracene .	20	2
6-*iso*Propyl-1:2-benzanthracene	17	11
5:6-*cyclo*-Penteno-1:2-benzanthracene (VI)	70	26
6:7-*cyclo*-Penteno-1:2-benzanthracene	10	7



VI.

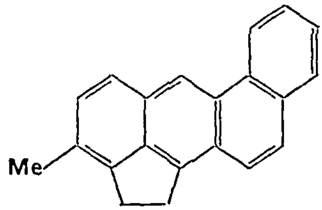
TABLE II.

Non-Carcinogenic Homologues.

3-Me-1:2-benzanthracene.
7-Me-1:2-benzanthracene.
2′-Me-1:2-benzanthracene.
3′-Me-1:2-benzanthracene.
2′:6:diMe-1:2-benzanthracene.
2′:7:diMe-1:2-benzanthracene.
3′:6-diMe-1:2-benzanthracene.
3:7-diMe-1:2-benzanthracene.
3-*iso*Propyl-1:2-benzanthracene.
7-*iso*Propyl-1:2-benzanthracene.
10-*iso*Propyl-1:2-benzanthracene.

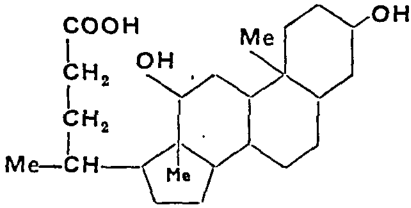
A systematic fractionation of 12 tons of coal tar pitch was carried out by Hieger, who finally obtained a few grams of a pure hydrocarbon having powerful carcinogenic properties. This was proved by synthesis to be 3:4-benzpyrene (V) by Cook, Hewett and Hieger J.C.S. 1933, 395). Results with animal experiments showed that 3:4-benzpyrene is the main carcinogenic constituent of coal tar. Schürch and Winterstein (Z. physiol. Chem. 1935, 236, 79) have not obtained tumours with a tetrahydrobenzpyrene in 150 days, or with 3′-methyl-3:4-benzpyrene in 270 days.

The most powerful carcinogenic agent yet discovered is methylcholanthrene (VII):



VII.

This substance was prepared independently by Wieland and Dane (Z. Physiol. Chem. 1933, 219, 240), and by Cook and Haslewood (Chem. and Ind. 1933, 38, 758) by dehydrogenation of dehydronorcholene (VIII) obtained from deoxycholic acid (IX)—a bile acid—by simple chemical changes:



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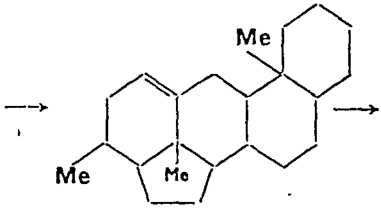


→ VII.

VIII.

The conversion of cholic acid into methylcholanthrene has been reported by Fieser and Newman (J. Amer. Chem. Soc. 1935, 57, 961, 1602). Considering the fact that cholic acid and deoxycholic acid are important acids of human bile, the carcinogenic property of methylcholanthrene is of particular significance in the ætiology of human cancer. There is no evidence so far, however, of the biochemical degradation of bile acids into methylcholanthrene. Cholanthrene is also highly carcinogenic, solutions of both it and its methyl derivative, when painted on the skin of mice in 0 3% benzene solution, producing epitheliomata The first tumours make their appearance after about 70–80 days (average). The two substances also produce sarcomata.

Morton, Clapp and Branch (Science, 1935, 82, 134) claim that they have produced malignant tumours in mice with two hydrocarbons, *s* triphenylbenzene, and tetraphenylmethane. Triphenylbenzene gave sarcomata in 20% of the mice tested in 250 days when injected *sub cutem* (Amer. J. Cancer, 1936, 26, 754). The carcinogenic activities of these two hydrocarbons are not of high order.

For fuller information on this subject the reader is referred to a comprehensive article by Cook, Haslewood, Hewett, Hieger, Kennaway and Mayneord on "Chemical Compounds as Carcinogenic Agents" (Report of the 2nd International Congress of Scientific and Social Campaign against Cancer, Tome I, 1936).

J. H. Q.

CARCLAZITE or **CARCLAZYTE.** A name suggested by J. H. Collins (The Hensbarrow Granite District, Truro, 1878) for the china-clay rock from which china-clay is prepared. So named from the Carclaze mine, near St. Austell, in Cornwall. L. J. S.

CARDAMOMS. The principal variety of cardamoms and that recognised for official purposes consists of the seeds obtained from *Elettaria Cardamomum* Maton, var. *minuscula* Burkhill (Fam. Zingiberaceæ), a reed like plant growing to a height of 4 m or more in the forests of Southern India, but also cultivated in Ceylon and on the Malabar Coast. Owing to the ease with which the seeds can be adulterated by the addition of seeds of other species of cardamoms or of other plants, both the British and American Pharmacopœias direct that they shall be retained in their fruits until required to be used. This has the advantage also of preventing the evaporation of the essential oil, for which the seed is employed. The plants yield a small harvest of fruits in their third year, a full crop for the next 6 or 7 years, and then begin to decay. The fruits are collected from August until April, though the largest quantity is gathered between October and December, the first fruits being both larger in size and better in quality. Generally, the fruits are air-dried, the slower the drying the better, as rapid drying causes the pods to break open and reduces their market value. The colour of the dried fruit should be a pale buff or greenish-buff, though artificially dried fruits may be darker. The fruits measure from about 6–20 mm. in length, the smaller ones being almost globular, whilst the longer ones are definitely ovoid or oblong three sided pods. Internally, the fruits contain six rows of seeds, a double row in each cell, and in good fruits the seeds approximate to about 70% of the total weight. The seeds are angular, and about 4 mm. long and 3 mm. broad. They vary in colour from pale to dark reddish brown, and are covered by a membranous aril. Cardamoms are strongly aromatic and possess an aromatic though somewhat pungent taste. They are used chiefly for culinary purposes in curry powder, sauces and cordials, and in medicine as a carminative.

Microscopic Appearance.—The seeds show the presence of numerous compound angular starch grains with 1–7 minute calcium oxalate crystals embedded in each mass. The outer epidermis consists of long narrow cells with moderately thick, straight, or slightly curved walls, and more or less pointed ends. The sclerenchymatous cells vary from reddish-brown in ripe seeds to yellow in unripe ones and each cell encloses a nodule of silica. These sclerenchymatous cells are not cleared with chloral hydrate, but, in the case of ripe seeds, they become almost black with alkali, and in that of the unripe seeds, reddish brown. The cells of the endosperm have thin walls and do not contain calcium oxalate crystals. Immediately beneath is a layer of thin-walled cells containing the volatile oil, but in powdered preparations these are frequently ruptured.

Chemical Composition.—C. Arragon (Ann. Falsif. 1915 8, 345) quotes the following analyses of two samples of cardamoms.

	Ceylon %	Malabar %
Water	7·8	9 3
Ash	11·65	4 6
Fat	2 1	1 8
Essential oil	3 3	6 3
Protein	14 2	11·7
Fibre	18·7	13 2
Reducing substances, starch, etc.	39 7	58 3

All figures except water are on the dry material.

The principal constituent of cardamoms is the essential oil, and probably the most satisfactory method of determining this is by the process of Cocking and Middleton (Quart. J. Pharm. 1935, 8, 435). The crushed seeds are mixed with a brine solution, distilled, and the vapours passed through the top of a condenser into a graduated tube, in which the oil is collected whilst the condensed water is returned to the distillation flask. An air inlet or outlet is placed in the circuit below the condenser, but above the tube in which the liquids are collected. These authors find no difference in the yield of oil from the whole or crushed seed, though commercial powdered cardamom contains rather less oil than the whole fruits. The fruits contain from 3·4 to 8 0% of oil. For further details of the oil, *see* CARDAMOMS, ESSENTIAL OIL OF.

Standards.—The "British Pharmacopœia" requires that the seeds shall contain not more than 3% of foreign organic matter and that their ash shall be not more than 6%. The

"United States Pharmacopœia" requires that not more than 5% of the ash shall be acid-insoluble.

Adulteration.—Cardamom husks are offered periodically in the drug market, and although these are not bought openly, they appear to find their way into commerce as an adulterant, and should be recognised by the pitted fibres and the spiral cells of the fibro-vascular bundles. They also show empty parenchymatous cells. Ceylon fruits derived from *E. Cardamomum*, var. *major* Thwaites, are regularly sold in the market and may be readily distinguished by the fact that they are long and not ovoid, by their shrivelled appearance and their dark greyish-brown colour. T. McL.

CARDAMOMS, ESSENTIAL OIL OF. The oil distilled from the whole fruits of *Elettaria Cardamomum* Maton, cultivated in Ceylon, Mysore, Travancore, and Cochin on the tea and rubber estates. The cardomom oil of commerce was formerly distilled from the wild cardamoms of Ceylon.

Composition.—The oil contains cineole, terpinenol, terpinene limonene, sabinene, and terpineol in the form of formic and acetic esters.

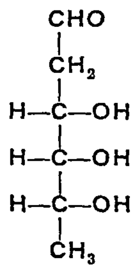
Characters.—It is a colourless or pale yellow oil, sp.gr. 0·923–0·945 at 15·5°, α^{20}_{D} +20° to +44°, n^{20}_{D} 1·461–1·467. Ester value 90–156. Soluble in 4 vols. 70% alcohol. It is used as a flavouring agent and has carminative properties. C. T. B.

CARDIAC GLYCOSIDES. The grouping together of the cardiotonic drugs is justified not only by their common characteristic action on the heart, but also by the close chemical relationship existing between all members of the group so far investigated. With the exception of the alkaloid erythrophleine and the toad poisons (*v. infra*), all these drugs are non-nitrogenous glycosides of plant origin yielding on hydrolysis various sugars and a number of structurally similar aglycones or "genins." Although apparently limited in number, plants yielding such glycosides are of wide geographical distribution; the majority belong to the natural order Apocynaceæ, but representatives of other families (*e.g.* Scrophulariaceæ, Ranunculaceæ, Liliaceæ) also contain cardiac glycosides. Extracts of some of these plants (*e.g. Digitalis*) have long been used in medicine as heart stimulants, while others (*e.g. Strophanthus*) furnish the arrow poisons of primitive races. The parts of the plant used for extraction of the glycosides vary in the different species, *e.g.* leaves and seeds (*Digitalis*), seeds (*Strophanthus*), bulbs (squill), flowers (lily of the valley), bark (ouabaio).

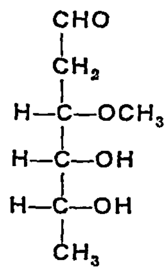
Only in a few cases (*e.g. Digitalis purpurea*, *D. lanata*, squill) have the original glycosides present in the various plants been isolated. These are water-soluble, often amorphous substances with a high glucose content, and are accompanied in the plant by specific enzymes capable of hydrolysing them to simpler glycosides. Unless the utmost precautions are taken to prevent enzyme action, hydrolysis occurs in varying degree during extraction. Hence crude extracts generally contain a complex mixture of amorphous and crystalline glycosides the composition of which varies with the conditions of extraction. For this reason much of the earlier literature on the cardiac glycosides is in a confused state. It is, however, possible, by controlled enzymatic action, to isolate a number of crystalline derived glycosides, and it is on these that most of the chemical work has been done. During this partial hydrolysis a considerable part of the physiological activity is lost. This may be due partly to decrease in solubility and partly to isomerisation of the aglycone by enzymatic action, *e.g.* isomerisation of cymarin to the inactive *allo*-cymarin in *Strophanthus Kombe* extracts (Jacobs, J. Biol. Chem. 1930, **88**, 519). The crystalline glycosides obtained from any one plant may be derived from one aglycone (*e.g. Strophanthus Kombe*) or from several (*e.g. Digitalis*).

Sugars of the Cardiac Glycosides.—Only a few simple sugars are represented in the carbohydrate part of the glycosides, the diversity of the latter being due to differences in the aglycones and to variation in the number and mode of attachment of the sugar residues. In addition to glucose and rhamnose, four sugars peculiar to the group have been found.

Digitoxose, $C_6H_{12}O_4$, has structure I (Micheel, Ber. 1930, **63**, [B], 347) and cymarose (II) is its methyl ether (Elderfield, J. Biol. Chem. 1935, **111**, 527). Sarmentose, $C_7H_{14}O_4$, is isomeric with cymarose (Jacobs and Bigelow, J. Biol. Chem. 1932, **96**, 355), but the configuration and position of the methoxyl group have not been determined. Digitalose, $C_7H_{14}O_5$, may be a methyl ether of rhamnose (Schmidt and Zeiser, Ber. 1934, **67**, [B], 2127). By mild hydrolysis of certain cardiac glycosides some hitherto unknown disaccharides have been obtained, *e.g.* strophanthobiose (from *Strophanthus*) and scillabiose (from squill).



I.



II.

STRUCTURE OF AGLYCONES.—Detailed investigations by various workers, particularly Jacobs and Tschesche and their collaborators, have thrown much light on the structure of the cardiac aglycones, and for a number of them structural formulæ have been advanced which are probably correct in all essential features. All the aglycones investigated are unsaturated hydroxy-lactones containing 23 carbon atoms (with the exception of scillaridin A, which has 24) and are structurally similar. The following list includes those for which fairly well established structural formulæ are available:

Strophanthidin, $C_{23}H_{32}O_6$.
Uzarigenin, $C_{23}H_{34}O_4$.
Digitoxigenin, $C_{23}H_{34}O_4$.
Gitoxigenin, $C_{23}H_{34}O_5$.
Digoxigenin, $C_{23}H_{34}O_5$.
Periplogenin, $C_{23}H_{34}O_5$.
Scillaridin A, $C_{24}H_{30}O_3$.

The structural similarity of the above C_{23} aglycones was shown by the conversion of *several pairs into identical compounds* by suitable reactions. In this way identity of the carbon skeleton was shown for:

(*a*) Periplogenin and strophanthidin (Jacobs, Elderfield, Grave and Wignall, J. Biol Chem 1931, **91**, 617).

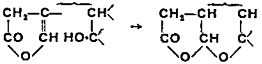
(*b*) Periplogenin and digitoxigenin (Jacobs and Elderfield, J. Biol Chem. 1931, **92**, 313).

(*c*) Periplogenin and uzarigenin (Tschesche, Z. physiol. Chem. 1933, **222**, 50).

(*d*) Digitoxigenin and gitoxigenin (Jacobs and Gustus, J. Biol. Chem 1930, **86**, 199)

(*e*) Digitoxigenin and digoxigenin (Tschesche and Bohle, Ber. 1936, **69**, 793).

In a series of investigations by Jacobs and his collaborators first on strophanthidin and later on other aglycones (in J Biol. Chem. 1927–1931) it was shown that all these compounds are lactones of γ-aldehydo acids, *i e* they are $\Delta^{\beta\gamma}$-γ-lactones. In each case the lactone group forms a separate side chain attached to the rest of the molecule by its β-carbon atom, and on the presence in it of a double bond depend the colour reactions with sodium nitroprusside and with Tollens' reagent (Jacobs and Hoffmann, J. Biol. Chem. 1925, **67**, 333), common to the aglycones and the parent glycosides. Under the influence of alkali the aglycones undergo a remarkable rearrangement giving the *iso*aglycones (Windaus and Hermanns, Ber. 1915, **48**, 993). This reaction, in which the lactone group and an adjacent tertiary hydroxyl are involved is formulated by Jacobs as follows.

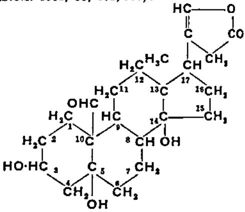


The *iso*aglycones, though still lactones, no longer possess the double bond of the original compound, into which they are reconverted by acid.

By selenium dehydrogenation of uzarigenin (Tschesche and Knick, Z. physiol Chem. 1933, **222**, 58) and of strophanthidin (Elderfield and Jacobs, J. Biol. Chem. 1934, **107**, 143), a hydrocarbon, $C_{18}H_{16}$, is obtained, identical with methyl *cyclo*pentenophenanthrene, obtained by a similar process from sterols. The fundamental similarity between the carbon skeleton of the cardiac aglycones and that of the sterols and bile acids suggested by this result has been finally established by the progressive degradation of certain aglycones to bile acid derivatives. Thus digitoxigenin can be degraded to ætiocholanic acid, $C_{20}H_{30}O_2$ (Jacobs and Elderfield, Science, 1934, **80**, 434), and uzarigenin to ætio*allo*cholanic acid, $C_{20}H_{30}O_2$ (Tschesche, Angew. Chem. 1934, **47**, 729; Z. physiol Chem. 1934, **229**, 219; Ber. 1935, **68**, [B], 7), both acids of known structure (*v.* BILE ACIDS). As a result of this work the carbon skeleton of the cardiac aglycones and the point of attachment of the lactone side chain are established beyond doubt.

Taking into consideration the results of other degradative experiments on the aglycones, *iso*-aglycones, and the numerous anhydro-derivatives produced by their partial dehydration it is possible to allot structural formulæ to the aglycones. This has been done for a number of them, and there is little doubt but that the formulæ are substantially correct, although the disposition of the hydroxyl groups may be in some cases uncertain. The results of X ray crystallographic examination of cardiac aglycones support the formulæ advanced (Bernal and Crowfoot, J.S C.I. 1934, **53**, 953).

For strophanthidin the following formula has been proposed (Tschesche and Knick, Z. physiol. Chem. 1934, **229**, 219; Jacobs and Elderfield, J. Biol. Chem. 1935, **108**, 497; Kon, J.S.C.I. 1934, **53**, 593, 956):



Strophanthidin contains one aldehyde group and three hydroxyls, of which two are tertiary. The hydroxyl at C_{14} is common to all the aglycones and is concerned in the formation of the oxide ring in the *iso*aglycones. The positions of the other hydroxyls vary in different aglycones and the aldehyde group at C_{10} in strophanthidin is frequently replaced by a methyl group. The structure of other members is as follows:

Periplogenin has a methyl at C_{10} in place of the aldehyde group in strophanthidin, the disposition of hydroxyls being the same (Tschesche and Knick, *l.c.*; Jacobs and Elderfield, *l.c.*).

Digitoxigenin has a methyl at C_{10} and hydroxyls at C_3 and C_{14} (Tschesche and Knick, *l c.*; Jacobs and Elderfield, *l c.*).

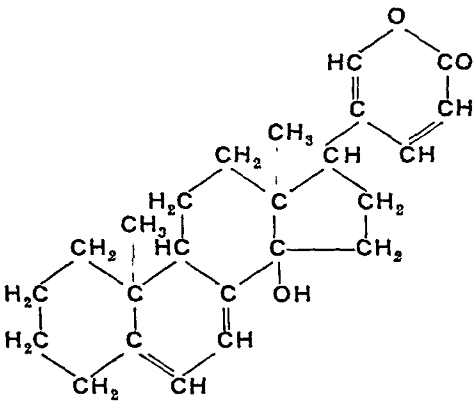
Gitoxigenin differs from digitoxigenin in having an additional hydroxyl at C_{16} (Tschesche and Knick, *l c.*; Jacobs and Elderfield, *l c.*), and *digoxigenin* is similar but has the additional hydroxyl at C_{11} (Tschesche and Bohle, Ber. 1936, **69**, [B], 793).

Uzarigenin is a stereoisomer of digitoxigenin (Tschesche and Bohle, Ber. 1935, **68**, [B], 2252).

Little work has been done on the stereochemistry of the various aglycones, but it would seem that uzarigenin belongs stereochemically

to the sterol series and the others investigated to the bile acid series (*cf.* Tschesche and Bohle Ber. 1935, 68, [B], 2252).

The structure of scillaridin A has been largely elucidated by Stoll and his collaborators (papers in Helv. Chim. Acta. 1933–1935). This aglycone, although an unsaturated lactone, does not give a coloration with sodium nitroprusside. It contains only one free hydroxyl which is tertiary and can interact with the lactone group, giving an *iso*aglycone. Reduction of scillaridin A or its anhydro-derivative causes opening of the lactone ring giving in the case of the latter a-scillanic acid, $C_{24}H_{40}O_2$, identical with *allo*-cholanic acid (*v.* Bile Acids, *also* Stoll, Hofmann and Helfenstein, Helv. Chim. Acta, 1935, 18, 644). Scillaridin A has thus the same carbon skeleton as the other aglycones, and the production from it of *allo*cholanic acid shows that it belongs to the sterol series. Moreover, the extra carbon atom of scillaridin A must be accommodated in the lactone grouping. Stoll and his collaborators embody their results in the following formula for scillaridin A, in which only the position of the double bonds is to be regarded as uncertain.



The positions of the points of attachment of the sugar residues in the various glycosides have not yet been determined although tentative suggestions have been made for certain members of the group (Jacobs, Stoll, and Fieser).

Physiological Action and Methods of Assay.—The cardiac glycosides are principally used in medicine for their action on the heart; they slow the beats and make them more powerful and regular so that the output is increased. Their first appearance in scientific medicine was about 1775, when Withering introduced the foxglove (*D. purpurea*), a plant which had for long been used as a popular remedy for dropsy. Chemical methods for the assay of plant extracts containing cardiac glycosides are unsatisfactory, and biological methods are usually employed. Of these the commonest is the "timeless" method of Straub (Arch. exp. Path. Pharm. 1916, 80, 52) based on the original procedure of Houghton (J. Amer. Med. Assoc. 1898) in which the minimum amount is determined which will arrest the frog's heart in systole (frog dose=F.D.). For a detailed account of the pharmacology of these compounds, *see* Weese, "Digitalis" (Leipzig, 1936). Tinctures of digitalis and strophanthus are standardised biologically in the British and United States "Pharmacopœias." In both cases the standards used are based on the standard preparations of digitalis leaves and ouabain adopted under international agreement (League of Nations).

Although the aglycone is undoubtedly the specific carrier of the activity, this activity is enormously increased, and in some respects modified by combination with sugars in the glycosides. The glycosides become irreversibly attached to the heart muscle, while the aglycones are distributed between the surrounding fluid and the muscle cells, so that a heart brought by them to systolic standstill may be restored by washing out. Accordingly, for therapeutic purposes the aglycones are practically worthless.

A few observations have been made on the effect of chemical change on the activity of the aglycones. Thus hydrogenation or hydrolytic opening of the unsaturated lactone ring practically destroys activity, as also does isomerisation to the *iso*aglycones. Changes affecting the lactone ring may be partly responsible for the frequently observed deterioration of digitalis, and other preparations on keeping.

Colour Reactions.—The cardiac glycosides give characteristic colorations with a mixture of concentrated sulphuric acid and glacial acetic acid containing a little ferric chloride (Keller, Ber. Pharm. Ges. 1895, 5, 275). An indigo-blue coloration in this reaction indicates the presence of digitoxose. A modification of the above is the so-called *Keller-Kiliani* reaction (Kiliani, Arch. Pharm. 1896, 234, 273). Ekkert (Pharm. Zentr. 1934, 75, 228) indicates a reaction for digitalis glycosides using various phenols. Cardiac glycosides generally give characteristic colours with Liebermann's cholesterol reagent (acetic anhydride+sulphuric acid). The following reactions are characteristic of the unsaturated lactone group in glycosides and aglycones:

Legal Reaction.—A deep red colour is developed with alkaline sodium nitroprusside (Jacobs and Hoffmann, J. Biol. Chem. 1926, 67, 609).

Tollens Reaction.—Aglycones and glycosides reduce ammoniacal silver nitrate solution (Jacobs and Hoffmann).

Baljet Reaction.—Alkaline picric acid produces a red orange colour (Baljet, Schw. Apoth.-Ztg. 1918, 56, 84).

The various strophanthins may be differentiated by their colour reactions with 80% sulphuric acid (*see* Ekkert, Pharm. Zentr. 1930, 71, 724; 1931, 72, 388).

Digitalis (Scrophulariaceæ).—Various species of *Digitalis* yield cardiac glycosides, but only *D. purpurea* is official in the "British Pharmacopœia" and "United States Pharmacopœia."

Digitalis purpurea Linn. (Foxglove).—Only the leaves are official, *Digitalis Folia*, "British Pharmacopœia"; *Digitalis*, "United States Pharmacopœia." The seeds have a similar action due, however, to different glycosides. Foxglove is a biennial plant and the activity of cultivated plants remains fairly constant up to the flowering period. The "British Pharmacopœia" prescribes leaves from plants beginning to flower. For culture, harvesting and con-

servation, *see* Newcomb (Amer. J. Pharm. 1917, 89, 147). Mature plants from different localities vary in their glycoside content (Straub, Arch. Pharm. 1917, 255, 198).

From the leaves and seeds a number of glycosides of varying complexity have been isolated, but it is probable that the list of such compounds is not yet complete. In the seeds the cardiac glycosides are accompanied by a number of saponins, *e g.* digitonin, gitonin. The first to isolate a crystalline preparation from the leaves was Nativelle (J. Pharm. Chim 1869, [iv], 9, 225; 1872, [iv], 16, 430; 1874, [iv], 20, 81) whose *digitaline cristallisée* consisted largely of the glycoside now known as *digitoxin*. Although a certain number of well-defined crystalline glycosides (*digitoxin, gitoxin, gitalin, digitalin*) were later isolated, the discrepancy between the activity of these compounds and that of the complete drug led Perrot and Goris (Bull Acad. Med 1909, 61, 681; 62, 97, Bull Sci. Pharmacol. 1931, 38, 7; Progres Med. 1933, 354) to the conclusion that the drug itself contained substances with a higher sugar content. The correctness of this view was established by Stoll and Kreis (Helv. Chim. Acta 1935, 18, 120), who isolated two amorphous glycosides which they consider to be compounds actually present in the leaves. Of these, *purpurea glycoside A* (activity 690 F.D./mg.) yields on enzymatic hydrolysis digitoxin and glucose, while *purpurea glycoside B* (activity 315 F.D./mg) gives similarly gitoxin and glucose. Table I gives a survey of the crystalline glycosides obtained from *D. purpurea*.

Glycoside	Sugars	Aglycone
Digitoxin	Digitoxose	Digitoxigenin
Gitoxin.	,,	Gitoxigenin
Gitalin	,,	Gitaligenin
Digitalin.	Digitalose+ Glucose	Digitaligenin

Digitoxin (digitaline crystallisée).—Extracted from leaves with alcohol. Nacrous angular plates, m p. 255°-257° (Windaus and Freese, Ber. 1925, 58, [B], 2506). Sparingly soluble in water, soluble in alcohol and chloroform. It is hydrolysed according to the following equation (Windaus and Stein, Ber. 1928, 61, [B], 2436):

$$C_{41}H_{64}O_{13}+3H_2O=\underset{\text{Digitoxigenin}}{C_{23}H_{34}O_4}+\underset{\text{Digitoxose}}{3C_6H_{12}O_4}$$

Digitoxigenin has m p. 250° and yields anhydro-derivatives with HCl (Smith, J.C.S. 1935, 1050). Digitoxose has m p. 112°, $[\alpha]^{20}_{5461}$ +55 6° (Smith, J.C.S. 1930, 508). For structure of aglycone and sugar, *see above*. Digitoxin gives the Keller-Kiliani reaction. Activity 200–300 F.D./mg.

Gitoxin.—First isolated in an impure state from an aqueous extract of the leaves by Kraft (Arch. Pharm. 1912, 250, 118) who described it under the name "anhydrogitalin." A glycoside obtained as a by-product by Merck in the manufacture of digitoxin was considered by Kiliani (Ber. 1915, 48, 335) to be different from anhydrogitalin, but was shown to be identical with it by Windaus and Schwarte (Ber. 1925, 58, 1515). These authors gave it the name gitoxin, by which it is now generally known. Gitoxin forms needles, m p 266°–269 °(Windaus), 285°, (Smith, Cloetta), very sparingly soluble in water, alcohol, or chloroform. Its purification and properties are described by Windaus and Schwarte (*l c*), Windaus, Westphal and Stein (Ber. 1928, 61, 1847), and Smith (J.C.S. 1931, 23). It hydrolyses according to the scheme:

$$C_{41}H_{64}O_{14}+3H_2O=\underset{\text{Gitoxigenin}}{C_{23}H_{34}O_5}+\underset{\text{Digitoxose}}{3C_6H_{12}O_4}$$

Gitoxigenin (structure above), has m p. 224°-225°, leaflets, and with alcoholic HCl yields digitaligenin (*see below*) by loss of $2H_2O$. Gitoxin gives the Keller-Kiliani reaction and is about half as toxic as digitoxin in the frog test. Cloetta's "bigitalinum crystallisatum" is identical with gitoxin. Activity *c.* 100 F.D /mg

Gitalin.—This leaf glycoside was described by Cloetta (Arch. exp. Path. Pharm. 1926, 112, 261) under the name "gitalinum crystallisatum." Needles, m.p. 245°–247°, much more soluble than gitoxin. It hydrolyses according to the following equation (Windaus, Arch. exp Path. Pharm. 1928, 135, 253; Jacobs and Gustus, J. Biol. Chem. 1928, 79, 555):

$$C_{35}H_{56}O_{12}+2H_2O=\underset{\text{Gitaligenin.}}{C_{23}H_{36}O_6}+\underset{\text{Digitoxose}}{2C_6H_{12}O_4}$$

Gitaligenin, m p. 222°, gives on acylation and reduction the same products as gitoxigenin. Windaus (*l c.*) considers it to be a hydrate of gitoxigenin. Gitalin gives the Keller-Kiliani reaction. Activity *c.* 110 F.D./mg.

Diginin.—Karrer ("Barell Festschrift," p. 238; Basle, 1936) isolated this inactive glycoside together with two as yet uncharacterised highly active substances from *D. purpurea* leaves. Diginin, colourless prisms, $[\alpha]^{20}_{D}$ −176°, although inactive, gives the colour with sodium nitroprusside characteristic of the $\beta\gamma$-unsaturated lactone group. It yields on hydrolysis digitoxose and an unidentified aglycone.

Digitalin.—The seeds of *D. purpurea* contain active glycosides which are accompanied by saponins (*e g.* digitonin, gitonin). Only one of these active principles has been recognised as an individual. This is the digitalin of Schmiedeberg (Arch. exp. Path. Pharm. 1874, 3, 27), which has since been investigated by Kiliani, who isolated it from the *Digitalis pur. pulv. germanicum* of Merck. He named it *digitalinum verum*, and showed that it gave on hydrolysis digitaligenin, glucose, and digitalose. The more recent work of Windaus (Nachr. Ges. Wiss Göttingen, 1927, 422) caused a revision of Kiliani's formula. It hydrolyses according to the following equation (Windaus, Westphal, and Stein, *l.c.*; Windaus and Haack, Ber. 1928, 61, 1849; 1929, 62, 475):

$$C_{36}H_{56}O_{14}+2H_2O$$
$$=C_{23}H_{34}O_5+C_6H_{12}O_6+\underset{\text{Digitalose}}{C_7H_{14}O_5}$$

$$\underset{\text{Gitoxigenin}}{C_{23}H_{34}O_5} \rightarrow \underset{\text{Digitaligenin}}{C_{23}H_{30}O_3}+2H_2O$$

Digitalin usually forms granules, m.p. 210°–217°. It is sparingly soluble in water (1 : 1,000) and readily so in alcohol. The saponins which accompany it in the seeds affect the solubility in some way, for the mixture of digitalin and saponins is readily soluble in water. Digitaligenin, m.p. 210°–212°, is not the primary product of hydrolysis, but results from the dehydration of initially formed gitoxigenin. Digitalose is a syrup (for constitution, see p. 381). Activity of digitalin *c.* 75 F.D./mg.

Digitalis lanata Ehrh.—A native of the Balkans, this plant is cultivated in Western Europe, and is now an article of commerce. The leaves are 3–4 times more active than *D. purpurea*. Smith (J.C.S. 1930, 508; 1931, 23) obtained from the leaves gitoxin and a new isomeric glycoside digoxin. Mannich, Mohs, and Mauss (Arch. Pharm. 1930, **268**, 453) found four glycosides all different from those of Smith. The nature of the *lanata* glycosides has, however, been made clear mainly by the work of Stoll and Kreis (Helv. Chim. Acta, 1933, **16**, 1049, 1085, 1390; 1934, **17**, 592). Fresh leaves were ground with a neutral salt to inactivate hydrolytic enzymes and the product extracted with ethyl acetate until the extract gave no Keller-Kiliani reaction. From the mixture of glycosides (digilanide) three isomorphous crystalline glycosides A, B, and C were obtained with activities 690, 540, and 640 F.D./mg respectively. The crude digilanide contains 46% A, 17% B, and 37% C. Unlike the *purpurea* glycosides, each of these substances contains an acetyl group. By controlled hydrolysis Stoll and Kreis were able to obtain a number of less complex glycosides as indicated in the following scheme:

$$\text{Digilanide A} \xrightarrow[\text{(−acetyl)}]{\text{alkali}} \begin{array}{c}\text{Deacetyldigilanide A}\\ \text{(=Purpurea Glycoside A)}\end{array} \xrightarrow[\text{(−glucose)}]{\substack{\text{enzymatic}\\ \text{hydrolysis}}} \text{Digitoxin.}$$

$$\text{Digilanide B} \xrightarrow[\text{(−acetyl)}]{\text{alkali}} \begin{array}{c}\text{Deacetyldigilanide B}\\ \text{(=Purpurea Glycoside B)}\end{array} \xrightarrow[\text{(−glucose)}]{\substack{\text{enzymatic}\\ \text{hydrolysis}}} \text{Gitoxin.}$$

$$\text{Digilanide C} \xrightarrow[\text{(−acetyl)}]{\text{alkali}} \text{Deacetyldigilanide C} \xrightarrow[\text{(−glucose)}]{\substack{\text{enzymatic}\\ \text{hydrolysis}}} \text{Digoxin.}$$

Mannich's lanadigin is a mixture of digilanides A, B, and C, in which C preponderates (Arch. Pharm. 1934, **272**, 5).

Digoxin.—First isolated by Smith (*l.c.*). It has m.p. 265° and is isomeric with gitoxin. On hydrolysis it yields 1 mol. digoxigenin, m.p. 222°, and 3 mols. digitoxose. It gives the Keller-Kiliani reaction, and is readily soluble in dilute alcohol. Activity 650 F.D./mg.

Strophanthus (Apocynaceæ).—Many strophanthus species are known to contain cardiac glycosides, but only the following seem to have been thoroughly investigated.

Strophanthus Kombé.—Fraser (Trans. Roy. Soc. Edin. 1887, **35**, 955) was the first to obtain an amorphous water-soluble active glycoside mixture from the seeds. Jacobs and Hoffmann (J. Biol. Chem. 1926, **67**, 609; **69**, 153) showed that all the glycosides are made up of strophanthidin combined with cymarose and varying amounts of glucose. They separated the crude mixture into an amorphous *k*-strophanthin soluble in water and a crystalline sparingly soluble *k*-strophanthin.

Crystalline k-*strophanthin* was shown by Jacobs and Heidelberger (J. Biol. Chem. 1922, **54**, 253) to consist of a mixture of chloroform-soluble cymarin and chloroform insoluble *k*-strophanthin-*β*.

Amorphous k-*strophanthin* is a mixture of glycosides derived from cymarin by addition of varying amounts of glucose (Jacobs and Hoffmann, *l.c.*).

Cymarin.—Crystallises in prisms, m.p. 138°–148°. It hydrolyses according to the scheme:

$$C_{30}H_{44}O_9 + H_2O = \underset{\text{Strophanthidin}}{C_{23}H_{32}O_6} + \underset{\text{Cymarose}}{C_7H_{14}O_4}$$

Strophanthidin has m.p. 171°–175° (for constitution of aglycone and sugar, see pp. 382 and 381). Cymarin also occurs in *Apocynum cannabinum* (*v. infra*). It has an activity of *c.* 1250 F.D./mg., whereas strophanthidin has only 400 F.D./mg. (Straub, Biochem. Z. 1916, **75**, 132).

k-*Strophanthin-β* has m.p. 150°–151°, and is readily soluble in water. It hydrolyses according to the equation:

$$C_{36}H_{54}O_{14} + 2H_2O = \underset{\text{Strophanthidin}}{C_{23}H_{32}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Cymarose}}{C_7H_{14}O_4}$$

k-Strophanthin-*β* is thus a gluco-cymarin. Activity 1300–1500 F.D./mg. (Straub, *l.c.*)

Jacobs (J. Biol. Chem. 1930, **88**, 519) found in extracts of *S. Kombé* seeds a third glycoside, allo*cymarin*, m.p. 145°, which was physiologically inactive. This substance is believed to owe its origin to enzymatic isomerisation of cymarin in the extraction process; it hydrolyses to cymarose and allo*strophanthidin*, m.p. 248°.

Strophanthus hispidus DC.—Jacobs and Hoffmann (J. Biol. Chem. 1928, **79**, 531) showed that the seeds yield a complex mixture of strophanthidin glycosides, of which cymarin forms a part. Tschesche (Ber. 1935, **68**, [B], 423), however, obtained a mixture of glycosides which could not be crystallised, but gave on hydrolysis anhydro- derivatives of two aglycones *hispidogenin*-A, $C_{23}H_{34}O_5$, and *hispidogenin*-B, $C_{23}H_{34}O_6$.

Strophanthus Emini.—The seeds contain a mixture of glycosides investigated by Jacobs and Bigelow (J. Biol. Chem. 1933, **99**, 521). The more readily hydrolysable glycosides were not isolated in crystalline form, but yielded on

hydrolysis strophanthidin and periplogenin, the aglycone of *periplocymarin* (see *Periploca græca*) From the more stable portion of the crude mixture a monoside, $C_{30}H_{46}O_{9}$, and a bioside, $C_{36}H_{56}O_{14}$, were isolated. Both of these are derived from an aglycone, which could only be isolated as its trianhydro derivative, isomeric, but not identical with trianhydroperiplogenin The monoside yields a sugar, $C_7H_{14}O_5$, identical or isomeric with digitalose (*see* p. 381) The bioside yields, in addition, glucose

Strophanthus gratus (=*Strophanthus glaber*), —Arnaud (Compt rend 1888, **107**, 1162, 1898, **126**, 346, 1208, 1280, 1684, 1873) obtained from the seeds the crystalline glycoside *ouabain*, which he first discovered in the roots and bark of the ouabaio tree (*Acolanthera Ouabaio*) of East Africa. The identity of the two products was finally established by Thoms (Ber. Pharm Ges. 1904, **14**, 104) who applied to it the name *g-strophanthin* to distinguish it from k-(*Kombé*)-*strophanthin* On account of its accessibility in a pure condition, ouabain has been adopted as a standard for the biological assay of strophanthus preparations. Purification and physical constants are described by Schwartze, Hann and Keenan (J. Pharm Exp Ther. 1929, **36**, 481) Plates, m.p. 185°. Hydrolyses according to the following equation (Jacobs and Bigelow, J Biol Chem 1932, **96**, 647)·

$$C_{29}H_{44}O_{12}+H_2O=\underset{\text{Ouabagenin}}{C_{23}H_{34}O_8}+\underset{\text{Rhamnose}}{C_6H_{12}O_5}.$$

Ouabagenin is very sensitive to acids and has only been crystallised in the form of anhydro derivatives A complete structural formula for ouabain has been put forward by Fieser and Newman (J Biol Chem 1936, **114**, 705) Activity 2,000 F D /mg. It is soluble in water and dilute alcohol, and insoluble in ether, chloroform or absolute alcohol. Ouabain gives characteristic colour reactions (Ekkert, Pharm Zentr. 1930, **71**, 724, 1931, **72**, 388)

Strophanthus sarmentosus DC —The seeds contain a mixture of glycosides from which by enzymatic hydrolysis glucose and *sarmentocymarin* are obtained (Jacobs and Heidelberger, J. Biol Chem 1929, **81**, 765) Sarmentocymarin, prisms, m p. 130°, is soluble in chloroform and sparingly so in water It hydrolyses very readily with acids to give *sarmentose*, $C_7H_{14}O_4$ (*see* p. 381), and *sarmentogenin*, $C_{23}H_{34}O_5$, prisms from dilute alcohol, m p. 265°–266° (anhydrous).

Apocynum (Apocynaceæ) —Canadian hemp (*Apocynum cannabinum*) has long been known to possess cardiotonic activity Taub and Fickewirth (Bayer, D R P 255537, 1912) were the first to isolate from it cymarin (see *S Kombé*) identified as a glycoside of strophanthidin by Windaus and Hermanns (Ber. 1915, **48**, 979, 991). Cymarin was also obtained from other species of *Apocynum* (*androsæmefolium, venetum*)

Nerium Oleander Linn. (Apocynaceæ) —Of the active glycosides obtainable from the leaves *oleandrin* (Windaus and Westphal, Nachr. Ges. Wiss. Gottingen, 1925, 78) has been definitely characterised. The glycoside *folinerin* (Flury and Neumann, Klin. Woch. 1935, **14**, 562) has been shown to be identical with oleandrin (Neumann, Ber. 1937, **70**, [B], 1547); Tschesche, *ibid.* 1937, **70**, [B], 1554).

Oleandrin.—Needles, m.p. 249°; hydrolyses according to the following equation (Neumann, *l c.*; Tschesche, *l c.*),

$$C_{32}H_{48}O_9+H_2O=\underset{\text{Oleandrigenin}}{C_{25}H_{36}O_6}+\underset{\text{Oleandrose}}{C_7H_{14}O_4}$$

Oleandrose has not yet been characterised. Oleandrigenin is a monoacetyl derivative of gitoxigenin, the acetyl group being attached to the C_{16} hydroxyl (Tschesche, *l c.*).

Oleandrin has activity 1,200 F.D /mg. (Flury and Neumann, *l.c.*). According to Neumann (*l c.*) oleandrin is accompanied in the leaves by another glycoside, *adynerin*, m p. 234°, which, like allocymarin (*see above*), is inactive.

Thevetia nereifolia (=*Cerbera Thevetia* Linn) (Apocynaceæ).—The nuts of the ahouai tree of the West Indies contain a mixture of glycosides, the main constituent being *thevetin*, $C_{29}H_{46}O_{13}$, m p. 193°, soluble in alcohol and sparingly so in water (Chen and Chen, J. Biol. Chem. 1934, **105**, 231; J. Pharm. Exp. Ther. 1934, **51**, 23). Activity 200 F D /mg. It is present in the nuts to the extent of 3 6–4% Little is known of the other glycosides, *nerifolin*, m p. 189°, and *ahouain*, m p. 144°, described by Chen and Chen

Periploca Græca (Asclepiadaceæ) —Lehmann (Arch. Pharm. 1897, **235**, 157) isolated from the bark of this tree a crystalline glycoside *periplocin*, yielding on hydrolysis a reducing sugar and an aglycone *periplogenin*. The drug has been thoroughly investigated by Jacobs and Hoffmann (J. Biol. Chem. 1928, **79**, 519), who showed that it contains a mixture of glycosides which yielded crystalline *periplocymarin* on enzymatic hydrolysis.

Periplocymarin, m.p. 138°–148°, yields on acid hydrolysis cymarose and *periplogenin*, $C_{23}H_{34}O_5$ According to Jacobs and Hoffmann, Lehmann's periplocin is to be regarded as a glucoperiplocymarin, $C_{36}H_{56}O_{13}$.

Uzara (Asclepiadaceæ).—The roots of certain *Gomphocarpus* species furnish the arrow poison of South East African tribes. Hennig (Arch. Pharm 1917, **255**, 382) was the first to isolate the principal glycoside *uzarin* in crystalline form Uzarin crystallises in needles, m.p. 200°–210°, is sparingly soluble in water, but soluble in dilute alcohol It hydrolyses according to the following equation (Windaus and Haack, Ber. 1930, **63**, 1377):

$$C_{35}H_{54}O_{14}+2H_2O=\underset{\text{Uzarigenin}}{C_{23}H_{34}O_4}+\underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Uzarigenin has only been isolated as its anhydro-derivative, $C_{23}H_{30}O_3$ (for constitution, *see* p 382). A second glycoside, *uzaren*, has been described by Grobel (Diss. Marburg, 1925).

Squill (Liliaceæ). The bulbs of *Scilla maritima* L. (=*Urginea maritima* Baker) were used in ancient times in the treatment of heart diseases, although the drug is mainly used to day for its expectorant properties. Present knowledge of the cardiac glycosides of squill is mainly due to the work of Stoll and his collaborators. The bulbs when extracted under conditions which minimise enzymatic action yield crystalline

scillaren A and amorphous *scillaren B* (Stoll, Suter, Kreis, Bussemaker and Hofmann, Helv. Chim. Acta, 1933, **16**, 703).

Scillaren A crystallises in leaflets, m.p. 270°. It gives no colour reaction with sodium nitroprusside. Acid hydrolysis proceeds according to the scheme:

$$\underset{}{C_{36}H_{52}O_{13}} = \underset{\text{Scillaridin A}}{C_{24}H_{30}O_3} + \underset{\text{Scillabiose}}{C_{12}H_{22}O_{10}}$$

Scillabiose may be further hydrolysed to 1 mol. glucose and 1 mol. rhamnose. Hydrolysis of scillaren A with the enzyme scillarenase gives an intermediate product *proscillaridin A* and 1 mol. glucose (Stoll, Kreis, and Hofmann, Z. physiol. Chem. 1933, **222**, 24).

Scillaridin A, prisms, m.p. 245°–250°, is really the anhydro- derivative of the unstable aglycone of scillaren A, removal of the sugar residue from the latter being accompanied by dehydration. The additional hydroxyl of the hypothetical aglycone is considered to be at C_5, and to it is attached the scillabiose residue in the glycoside (Stoll, Helfenstein, and Hofmann, Helv. Chim. Acta, 1935, **18**, 644). Scillaren A has an activity of *c.* 1,000 F.D./mg.

Scillaren B represents a mixture of glycosides, and its composition is not yet known. It is more readily soluble in water than scillaren A, and has an activity of 2,000 F.D./mg.

Convallaria majalis (Liliaceæ).—From the flowers of lily of the valley Walz (Jb. prakt. Pharm. 1858, **12**, 302) obtained two amorphous glycosides, *convallamarin* and *convallarin*, of which only the first was active. Neither of these products was homogeneous. Karrer (Helv. Chim. Acta, 1929, **12**, 506) was the first to obtain a crystalline cardiac glycoside *convallatoxin*, needles, m.p. 212°–213°, activity *c.*3,000 F.D./mg., and for which Tschesche (Ber. 1936, **69**, 459) established the formula $C_{29}H_{42}O_{10}$. It hydrolyses to 1 mol. rhamnose and *convallatoxigenin*, $C_{23}H_{32}O_6$, apparently identical with strophanthidin (Fieser and Jacobsen, J. Amer. Chem. Soc. 1937, **59**, 2335).

Adonis (Ranunculaceæ).—Various *Adonis* species contain cardiac glycosides (*see* Hatcher and Haag, J. Pharm. Exp. Ther. 1933, **47**, 217), but only *Adonis vernalis* has been examined to any extent. The first detailed chemical investigation of the drug was made by Heyl, Hart and Schmidt (J. Amer. Chem. Soc. 1918, **40**, 436). Karrer (D.R.P. 480410, 1926; 484361, 1927) and Mercier and Mercier (Rev. Pharmacol. 1927, **1**, 1) isolated a mixture of water soluble and water sparingly soluble glycosides, *adonidoside* and *adonivernoside* having respectively 600 and 300 F.D./mg.

Helleborus (Ranunculaceæ).—From the roots of *Helleborus niger* and *viridis*, Husemann and Marmée (Ann. Chem. Pharm. 1865, **135**, 55) isolated a semi-crystalline mixture of glycosides which they considered to consist of *helleborein* and *helleborin*. The active helleborein was investigated chemically by Thaeter (Arch. Pharm. 1897, **235**, 414) and Sieburg (*ibid.* 1913, **251**, 154), but according to Karrer ("Barell Festschrift," p. 243; Basle, 1936) this material was not homogeneous. Karrer (D.R.P. 605073, 1933) isolated from *H. niger* the crystalline homogeneous *hellebrin* $[\alpha]_D^{20°}$ −23°, activity *c.*3,000 F.D./mg. It gives no colour with sodium nitroprusside.

Antiaris toxicaria Lesch. (Moraceæ).—The latex of the upas tree furnishes the arrow poison of native races in the Malay Archipelago. Kiliani (Ber. 1910, **43**, 3574) obtained from it *α-antiarin*, plates, m.p. 220°–225°, and *β-antiarin*, needles, m.p. 206°–207°. Both glycosides have powerful digitalis-like activity, and yield the same aglycone antiarigenin. The sugar component of α-antiarin is antiarose, isomeric with rhamnose, which is obtained from β-antiarin. These compounds have been investigated by Tschesche (Ber. 1936, **69**, 1377), who established the formulæ of both glycosides as $C_{29}H_{42}O_{11}$. Hydrolysis gives dianhydroantiarigenin, $C_{23}H_{28}O_5$, m.p. 200°–205°. The true aglycone, antiarigenin, could not be isolated. α- and β-antiarin give a positive reaction with sodium nitroprusside.

Cerbera Odollam contains a crystalline glycoside, *cerberin*, m.p. 190°–192°, not identical with thevetin (Plugge, Arch. Pharm. 1896, **231**, 10).

Cerbera tanghinia (=*Tanghinia venenifera*) fruits yield *tanghinin*, m.p. 182° (Arnaud, Compt. rend. 1889, **108**, 1255; 1890, **109**, 701), which may not be a glycoside.

Urechites suberecta is known as an arrow poison in the West Indies. It contains two crystalline glycosides, *urechitin* and *urechitoxin* (Bowrey, J.C.S. 1878, **33**, 252).

Adenium Boehmianum Schinz, a South West African arrow poison, contains *echujin* (Boehm, Arch. exp. Path. Pharm. 1899, **26**, 165).

Coronilla species contain in seeds and stems a glycoside, *coronillin*, with an activity 200 F.D./mg. (Schlagdenhauffen and Reeb, Arch. Pharmacodynam. 1897, **3**, 1).

Evonymus atropurpureus contains a crystalline glycoside *evonymin* with an activity 300–400 F.D./mg. (*see* Schmiedeberg, Arch. exp. Path. Pharm. 1883, **16**, 149).

Cheiranthus (Cruciferæ), wallflower species, contain a glycoside, *cheiranthin*, with an activity 400 F.D./mg. (Jaretzky and Wilcke, Arch. Pharm. 1932, **270**, 81).

The following plants are alleged to contain cardiac glycosides which have not been properly investigated: *Viscum album* (mistletoe), *Nymphaea alba*, *Rabelaisia philippinensis*, *Calotropis procera*, *Pachypodium scalli*, *Cryptostegia madagascariensis*, *Gratiola officinalis*, *Ilex opaca*, *Bowiea volubilis*, and the "pakuru-neara" tree of South America. For details, *see* Weese ("Digitalis," Leipzig, 1936).

Bibliography.—For detailed accounts of the cardiac glycosides, the following modern reviews are recommended: Jacobs, Physiol. Reviews, 1933, **13**, 222; Kon, Ann. Rep. Chem. Soc. 1934, **31**, 218; Stoll, "Cardiac Glycosides," London, 1937; Weese, "Digitalis," Leipzig, 1936.

Toad Poisons.

The secretions of the parotid glands of many species of toads contain substances of powerful physiological activity very similar to that of the cardiac glycosides. In addition there occur a number of basic substances, *e.g. bufotenine*,

bufotenidine, *bufothionine*, *adrenaline*, which, however, have no digitaloid properties (Wieland, Konz and Mittasch, Annalen, 1934, **513**, 1; Wieland and Wieland, *ibid.* 1937, **528**, 234; Jensen and Chen, J. Biol. Chem. 1936, **116**, 86). The cardioactive substances (*bufotoxins*) are made up of "genins" combined with suberyl arginine. There is still some doubt as to whether the "genins" ever occur in the secretions in the free state. Since Tschesche and Offe (Ber. 1935, **68**, [B], 1998) and Jensen (J Amer. Chem Soc. 1935, **57**, 2733) obtained *methyl cyclopentenophenanthrene by dehydrogenation of cinobufagin* the "genin" from the Chinese toad, it is practically certain that the original suggestion of Wieland and Alles (Ber. 1922, **55**, 1789) that the "genins" have a structure similar to the bile acids is correct. The toad poisons contain a lactone ring but do not give the sodium nitroprusside reaction of the digitalis and strophanthus glycosides

All toad poisons appear to be structurally similar to each other and to the cardiac glycosides (particularly the squill glycosides). They were known and used in European medicine before the introduction of digitalis (Schroeder *1672*; Dale 1692).

Bufo vulgaris (=*Bufo bufo bufo*).—From the skin of the common European toad, Wieland and Weil (Ber. 1913, **46**, 3315) isolated *bufotalin*, $C_{26}H_{36}O_6$, which was later shown to be derived from *bufotoxin*, $C_{40}H_{62}O_{11}N_4$, in which it is combined with suberylarginine (Wieland and Alles, *l.c.*). Hydrolysis of bufotoxin with strong acid proceeds according to the scheme:

$$C_{40}H_{62}O_{11}N_4 \rightarrow \underset{\text{Bufotalien}}{C_{24}H_{30}O_3} + \underset{\text{Suberylarginine}}{C_{14}H_{26}O_5N_4} + CH_3COOH + H_2O$$

Bufotalien is thus the anhydro-derivative of a genin, $C_{24}H_{32}O_4$, whose acetyl derivative is bufotalin By reduction of bufotalien and opening of the lactone ring, an acid $C_{24}H_{40}O_2$ was obtained isomeric with cholanic acid (*see* bile *acids*) (*Wieland, Hesse and Meyer, A. 1932, 493*, 272). Bufotoxin is described as *vulgarobufotoxin* by Chen, Jensen and Chen (J. Pharm. Exp. Ther. 1933, **47**, 307) who were unable to find any free bufotalin in the skin and secretion.

Bufo japonicus (=*B. formosus*=*B. gama*).—The Japanese toad yields *gamabufotoxin*, $C_{38}H_{60}O_{10}N_4$, hydrolysed to *gamabufogenin*, $C_{24}H_{34}O_5$, and suberylarginine (Wieland and Vocke, A. 1930, **481**, 215; *cf.* however, Chen and Chen, J. Exp. Pharm. Ther. 1933, **49**, 26; Kotake, A. 1928, **465**, 11).

Bufo gargarizans (=*B. chinensis*).—The dried parotid secretion of the Chinese toad forms the drugs "Senso" and "Ch'an Su." From these drugs is obtained *cinobufotoxin*, $C_{43}H_{64}O_{12}N_4$, hydrolysing to *cinobufagin*, $C_{25}H_{32}O_6$, and *suberylarginine (Jensen and Chen, J. Pharm.* Exp. Ther. 1931, **43**, 13; Jensen and Evans, J. Biol. Chem. 1934, **104**, 307).

Bufo arenarum yields *arenobufagin*, $C_{25}H_{34}O_6$, and *arenobufotoxin*, $C_{25}H_{34}O_6 \cdot C_{14}H_{26}O_5N_4$, probably a compound of the former with suberylarginine. Both have digitalis-like action (Chen, Jensen and Chen, J. Pharm. Exp. Ther. 1933, **49**, 1).

Bufo viridis viridis (European green toad) yields *viridobufotoxin*, $C_{23}H_{34}O_5 \cdot C_{14}H_{26}O_5N_4$(?), which may be a compound of *viridobufagin*, $C_{23}H_{34}O_5$, and suberylarginine (Chen, Jensen and Chen, *ibid.* 1933, **49**, 14).

Bufo marinus (=*Bufo agua*)—Gives *marinobufagin*, $C_{24}H_{32}O_5$, and *marinobufotoxin*, $C_{38}H_{58}O_{10}N_4$, its compound with suberylarginine (Jensen and Chen, *ibid.* 1931, **43**, 13) Marinobufagin is identical with *bufagin*, the *first crystalline cardioactive compound isolated* from toad venom by Abel and Macht (J. Pharm. Exp. Ther. 1911–1912, **3**, 319).

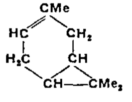
Chen and Chen (J. Pharm. Exp. Ther. 1933, **49**, 503) also describe digitalis like substances from the parotid secretions of *B. regularis*, *B. valliceps*, *B fowleri*, *B. alvarius*, *B. quercicus*, and *B. americanus*. A. R. T.

CARDIAZOL. Pentamethylene tetrazol. M.p. 56°–58° Readily soluble in water. The solution can be sterilised. Cardiac stimulant, B P C 1934

CARDOL, $C_{32}H_{52}O_4$ (?), a phenolic constituent of cashew nut shell oil (*v.* ANACARDIUM NUT). J. L. and E. L.

CARDOX CARTRIDGES, used in fiery mines, are cartridges of solid carbon dioxide heated *in situ* by a suitable contrivance.

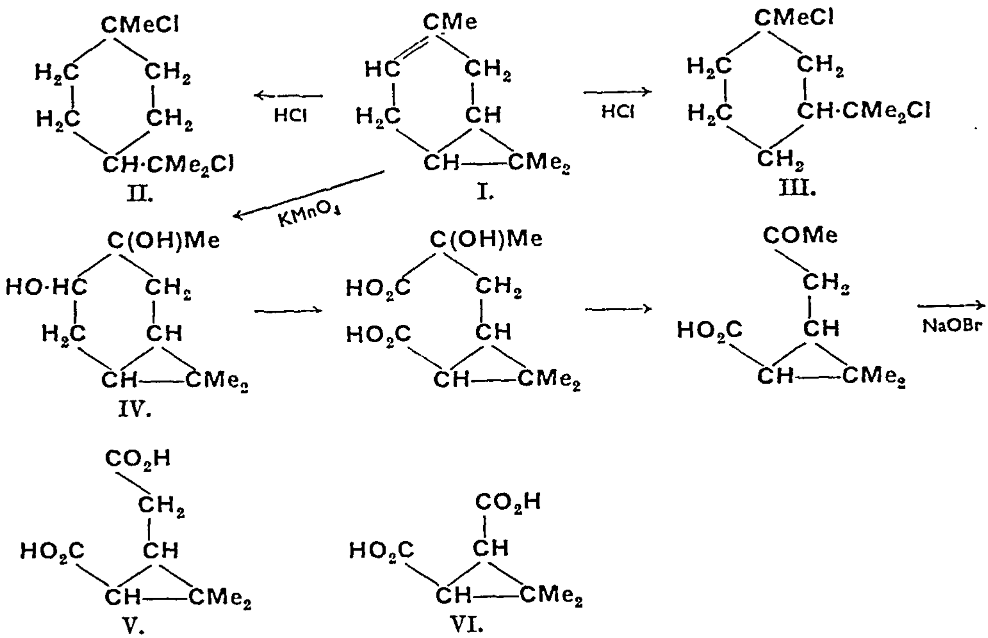
Δ^3-CARENE.



The dicyclic hydrocarbon, *d*-Δ^3-*carene*, $C_{10}H_{16}$, *b.p. 170°/760 mm.*, d_{15}^{15} *0 8688*, n_D^{23} 1·4675, $[\alpha]_D$ +7 69°, forms the main constituent of Indian turpentine from the oleo resin of *Pinus longifolia* (Simonsen, J.C.S. 1920, **117**, *570; 1923, 123, 549; 1928, 359; 1929, 305*), and its occurrence has been observed in a number of other oils (Simonsen, Indian Forest Rec. 1923, **10**, 56; Panicker, Rao, and Simonsen, J. Indian Inst. Sci. 1926, **9A**, 137; Rao and Simonsen, J.C.S. 1925, **127**, 2494; Wienhaus and Schmidt, Schimmel's Report, 1928, p. 101; Semmler and von Schiller, Ber 1927, **60**, [B], 1591; Aschan, Annalen, 1928, **461**, 1; Krestinsky, Liverovsky and Malmberg, J. pr. Chem. 1931, [ii], **129**, 97). The hydrocarbon is readily identified by the preparation of the sparingly soluble *nitrosate*, m p. 147 5°; according to Lagache (*Bull. Inst. Pin, 1927, 233*) it yields an unstable *nitrosochloride*, m.p. 101°–102°. On catalytic hydrogenation the saturated hydrocarbon *carane*, $C_{10}H_{18}$, is obtained (*Krestinsky and Solodki, J. pr. Chem.* 1930, **126**, [ii], 14) prepared originally by Kishner (J. Russ. Phys. Chem. Soc. 1911, **43**, 1132) by the action of alkali on 1-carone hydrazone.

The constitution of *d*-Δ^3-carene (I) has been established (i) by its conversion with hydrogen chloride into a mixture of *dipentene* and

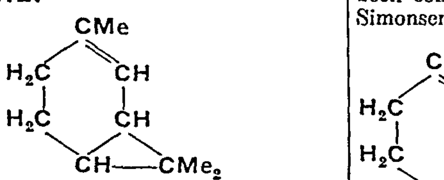
sylvestrene dihydrochlorides (II and III), and (ii) by its oxidation with potassium permanganate when the reaction proceeds in accordance with the scheme given below:



Homocaronic acid (V) has been prepared synthetically by Owen and Simonsen (J.C.S. 1933, 1225) and *caronic acid* (VI) by Perkin and Thorpe (*ibid.* 1898, 75, 48).

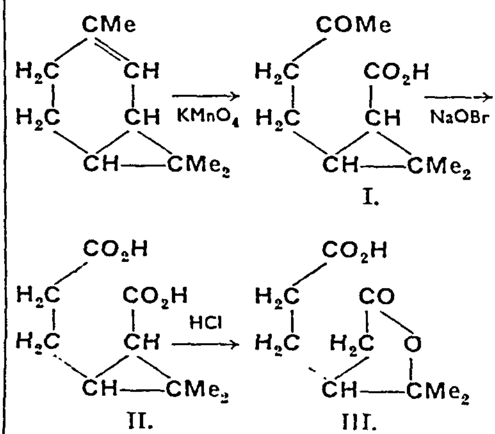
On oxidation with hydrogen peroxide *d*-Δ^3-carene yields a *glycol*, m.p. 90°–91° (Pillai and Simonsen, J.C.S., 1928, 359) isomeric with that, m.p. 69°–70° (IV), prepared by the action of potassium permanganate. The products of the auto-oxidation of the hydrocarbon in the presence of cobalt resinate have been investigated by Owen and Simonsen (J.C.S. 1931, 3001) and form a complex mixture. On exposure to the air the hydrocarbon oxidises very rapidly and this property renders it somewhat less valuable than pinene for use as a thinner in paints. J. L. S.

Δ^4-CARENE.



The dicyclic hydrocarbon, *d*-Δ^4-*carene*, $C_{10}H_{16}$, b.p. 165·5°–167°/707 mm., d^{30}_{30} 0·8552, n^{30}_D 1·474, $[\alpha]_D$ +69·2°, occurs in the essential oil from the grass *Andropogon Iwarancusa* Jones (Simonsen, J.C.S. 1921, 119, 1644; 1922, 121, 2292), in the oil from *Pinus sylvestris* (Semmler and von Schiller, Ber. 1927, 60, [B], 1591), in Finnish and Swedish turpentines (Aschan, Annalen, 1928, 461, 1; Wienhaus and Schmidt, Schimmels Report, 1928, p. 101), and in the oil from *Dacrydium Franklinii* (Penfold and Simonsen, J. Proc. Roy. Soc. New South Wales, 1929, 63, 95). The hydrocarbon has been prepared synthetically by the dehydration of 1-carol (Menon and Simonsen, J. Indian Inst. Sci. 1927, 10A, 4). No crystalline derivatives have been described.

The structure of the hydrocarbon is proved (*a*) by its fission with hydrogen chloride to yield a mixture of dipentene and sylvestrene hydrochlorides (*cf.* *d*-Δ^3-carene), and (*b*) by its oxidation with potassium permanganate to d-1:1-*dimethyl-2-γ-ketobutyl*cyclo*propane-3-carboxylic acid* (I) (*semicarbazone*, m.p. 182°–183°), which by further oxidation with sodium hypobromite gives d-3-*carboxy*-1:1-*dimethyl*cyclo*propane-2-propionic acid* (II), m.p. 104°–105°. The structure assigned to the latter acid, based originally on its conversion into *homoterpenylic acid* (III) by the action of hydrochloric acid, has been confirmed by its synthesis by Owen and Simonsen (J.C.S. 1932, 1424; 1933, 1223).



J. L. S.

CARMINAZARIN, an oxidation product of carminic acid.

CARMINIC ACID, the colouring matter of cochineal.

CARMOISINE. Syn for *Azorubin*. From naphthionic acid diazotised and coupled with a naphtholsulphonic acid NW.

CARNALLITE. Hydrated double chloride of potassium (KCl 26 8%) and magnesium, $KCl\,MgCl_2,6H_2O$. It occurs abundantly in the uppermost layers (" carnallite zone ") of the beds of *abraum salts* in the Prussian salt deposits, and is the chief commercial source of potassium chloride. It is also found at Wittelsheim in Upper Alsace, and in the potash salt basin of New Mexico and Texas. The mother-liquor, remaining after the potassium chloride has crystallised out, contains traces of bromine and rubidium, the former of which is a valuable by product. Thallium has also been detected in traces. When pure, the mineral is colourless and water-clear, but it is often coloured yellowish or reddish by intermixed impurities. Red carnallite owes its colour and metallic sheen (resembling that of sunstone) to the presence of minute scales of hæmatite. Crystals are rare ; they are orthorhombic, and have the form of six-sided pyramids with numerous well-developed faces. Owing to the extreme deliquescence of the salt, crystals must be preserved in sealed vessels. Carnallite and bromcarnallite, in which bromine takes the place of chlorine in the above formula, have been prepared artificially from suitable solutions containing a large excess of magnesium chloride and at a temperature of over 25°. L. J. S.

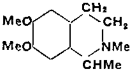
CARNAÜBIC ACID. This name was assigned by Sturcke (Annalen, 1884, 223, 306) to an acid, m p. 72 5°C., which he isolated from carnauba wax, and regarded as an isomer of lignoceric acid, $C_{23}H_{47}COOH$. the same acid was reported to be present in wool wax by Darmstadter and Lifschütz (Ber. 1896, 29, 618). In the light of our present knowledge concerning waxes it is highly probable that Sturcke's " carnaübic acid " was a mixture of *high-molecular fatty acids, among which n*-tetracosoic (lignoceric) acid may be included the fraction of m p. 72°–73° from the wool wax acids also appears to be a mixture of acids, among which an acid (in all probability not identical with any vegetable-wax acid) having 25, 26, or 27 carbon atoms (possibly with a branched chain) predominates (Abraham and T. P. Hilditch, J S C.I 1935, 54, 398T). The term " carnaubic acid " must therefore be regarded as obsolete. E. L.

CARNAÜBYL ALCOHOL. M p. 68°–69°C., was isolated from the saponification products of wool wax by Darmstädter and Lifschütz (Ber. 1896, 29, 2890) , since it yielded " carnaübic acid " (*q.v.*) on oxidation, the formula $C_{24}H_{49}OH$ was attributed to it. The existence of this alcohol as an individual was questioned by F. Röhmann (Biochem. Z. 1916, 77, 298; *cf.* Drummond and Baker, J.S.C.I. 1929, 48, 232T) whose work suggests that the product examined by the older workers may have been a mixture of alcohols (impure ceryl alcohol ?) ; on the other hand, an alcohol not of the ordinary even numbered fatty series may be in question. The name " carnaübyl alcohol " is misleading and should be discarded, since the tetracosoic acid present in carnaüba and other vegetable waxes is the n-C_{24} acid (*lignoceric acid*). E. L.

CARNEGINE, $C_{13}H_{19}O_2N$ (I), was isolated by Heyl (Arch. Pharm. 1928, 266, 668) from *Carnegia gigantea* (*Cereus giganteus*) (American Cactaceæ). Spath and Kuffner (Ber. 1929, 62, 2242) have shown that (I) is identical with the alkaloid *pectenine* previously isolated from *Cereus pecten aboriginum* Engelm by Heyl (Arch Pharm. 1901, 239, 459). For extraction *cf* Heyl (*l.c.* 1928). (I) is a colourless oil, b p 170°/1 mm , slowly decomposing under atmospheric influence; it cannot be crystallised.

B HCl, needles, m.p. 207° (Spath 210°–211°) from $CHCl_3$ Et_2O, easily soluble in H_2O, sparingly soluble in absolute EtOH ; B HBr, small needles, m p. 228°, from alcohol ; B $HAuCl_4$, yellow plates, from dilute EtOH ; the *picrate*, m p. 212°–213°, from MeOH ; the *methiodide*, m.p 210°–211°, from MeOH.

Spath (Ber. 1929, 62, 1021) has put forward the following constitution for (I) and has established it by synthesis :



I.

(I) therefore is related to the anhalonium alkaloids , it has also been obtained by methylation of the alkaloid *salsoline* (Orekhov and Proskurnina, Ber. 1934, 67, 878). Although (I) contains an asymmetrical carbon-atom, the alkaloid and its salts are optically inactive (*cf.* Schoepf and Bayerle, Annalen, 1934, 513, 190). For pharmacological action of (I) (Heyl, *l c.* 1901 and 1928), and Mogilewa (Arch. exp. Path Pharm 1903, 49, 137). *Schl*

CARNELIAN *v.* CHALCEDONY.

CARNINE was the name given to a basic substance isolated from meat extract by Voit (Weidel, Annalen, 1871, 158, 353) ; it occurs also in beer yeast extract (Schutzenberger, Chem. Zentr. 1877, 73), in the muscle of some fresh-water fish and frog's flesh (Krukenberg and Wagner, *ibid.* 1884, 107), and in beet juice (E O. von Lippmann, Ber. 1896, 29, 2645). Carnine crystallises in chalk-white druses, is sparingly soluble in cold, readily so in hot, water, insoluble in alcohol or ether ; it forms a crystalline *hydrochloride* and *platinichloride*, and a sparingly soluble compound with silver nitrate (Weidel, *l.c.*).

Haiser and Wenzel (Monatsh. 1908, 29, 157) have shown that carnine is an approximately equal molecular mixture of hypoxanthine and *inosine*, $C_{10}H_{12}O_5N_4$, and the two were separated by the action of acetic anhydride which converts the inosine into the *acetate*, $C_{10}H_9O_2N_4(OAc)_3$, m.p. 236° (decomp). Inosine crystallises in

silky needles, m.p. 215° (decomp.), $[\alpha]_D^{18^\circ} -49\cdot2^\circ$, and 100 c.c. of aqueous solution saturated at 20° contains 1·615 g.. When inosine is hydrolysed by sulphuric acid it yields hypoxanthine and a *pentose*, originally termed *carnose* by Levene and Jacobs (Ber. 1909, **42**, 2102, 2474), and afterwards identified with *d-ribose*.

M. A. W. and W. V. T.

CARNITES. [Derivatives of pyridine bases etc., used as dispersing and wetting-out agents.

CARNITINE, $C_7H_{15}O_3N$, a base first found in Liebig's extract of meat in 1905 by Gulewitsch and Krimberg (Z. physiol. Chem. 1905, **45**, 326), is present in the fresh muscle of many mammals (ox, 0·03% ; horse, 0·17% ; sheep, 0·19% (Smorodinzew, *ibid.* 1913, **87**, 12 ; 1914, **92**, 221) ; Strack, Wördehoff, Neubaur, and Geissendörfer (*ibid.* 1935, **233**, 189) give 0·1–0·2% for ox), and in other organs. It is most conveniently prepared from meat extract from which yields of from 1·3 to 1·8% can be obtained (Gulewitsch and Krimberg, *l.c.* ; Kutscher, Z. Nahr. Genussm. 1905, **10**, 528 ; Strack, Wördehoff, and Schwaneberg, Z. physiol. Chem. 1936, **238**, 183). Its identity with the base *novaine*, obtained by Kutscher (*l.c.*) from Liebig's extract, was proved by Krimberg (Z. physiol. Chem. 1908, **55**, 466 ; Engeland, Ber. 1909, **42**, 2457).

The free base forms a syrup easily soluble in water and alcohol and reacts alkaline. The *hydrochloride*, $C_7H_{15}O_3N{\cdot}HCl$, forms hygroscopic crystals ; $[\alpha]_D = -20\cdot9^\circ$ (c=10 in dilute HCl). The *nitrate*, $C_7H_{15}O_3N{\cdot}HNO_3$, crystallises in needles. The *platinichloride*, $(C_7H_{15}O_3N)_2{\cdot}H_2PtCl_6$, forms orange-red prisms, m.p. 214°–218° (decomp.). The *aurichloride*, $C_7H_{15}O_3N{\cdot}HAuCl_4$, forms citron yellow needles and orange needles or prisms, m.p. 153°–154°. There are two *double salts with mercuric chloride*, $C_7H_{15}O_3N{\cdot}2HgCl_2$, *from the free base and alcoholic mercuric* chloride, m.p. 204°–205°, is sparingly soluble and crystallises fairly readily ; in presence of excess of HCl, $C_7H_{15}O_3N{\cdot}HCl{\cdot}6HgCl_2$, m.p. 211°–215°, is formed as an oil crystallising with difficulty (Gulewitsch and Krimberg, *l.c.*; Krimberg, Z. physiol. Chem. 1907, **50**, 361). *Carnitine ethyl ester*, $C_9H_{19}O_3N$, is formed when an alcoholic solution of carnitine and hydrochloric acid is evaporated, and was mistaken by Kutscher for a new base from meat extract under the name *oblitine* (Kutscher, *l.c.* ; Krimberg, Z. physiol. Chem. 1907, **53**, 514 ; 1908, **56**, 417). The chemical and physiological properties of carnitine are reviewed by Gulewitsch (1927, A, 788).

Constitution of Carnitine.—On heating with baryta carnitine gives trimethylamine and crotonic and succinic acids (Gulewitsch and Krimberg, Z. physiol. Chem. 1905, **45**, 326) ; on reduction with phosphorus and hydriodic acid Willstätter's (Ber. 1902, **35**, 584) *γ-butyrotrimethylbetaine*

$$\begin{array}{lr} CH_2{\cdot}CH_2 & \text{—}CO \\ | & | \\ CH_2{\cdot}NMe_3 & {\cdot}O \end{array}$$

is formed (Krimberg, Z. physiol. Chem. 1907, **53**, 514) ; oxidation with calcium permanganate gives *β-homobetaine*

$$\begin{array}{lr} CH_2 & \text{———}CO \\ | & | \\ CH_2{\cdot}NMe_3 & {\cdot}O \end{array}$$

(Engeland, Ber. 1909, **42**, 2457) ; on heating with sulphuric acid at 130° carnitine loses a molecule of water giving an unsaturated betaine *apocarnitine* (*v. infra*). Carnitine is probably a hydroxy derivative of a trimethylbetaine. Two formulæ advanced by Krimberg (Z. physiol. Chem. 1907, **53**, 514) represented carnitine as either α- or β-hydroxy-γ-butyrotrimethylbetaine,

$$\begin{array}{lr} CH_2{\cdot}CH(OH){\cdot}CO \\ | \qquad\qquad / \\ CH_2{\cdot}NMe_3{\cdot}O \end{array} \quad \text{or} \quad \begin{array}{lr} CH(OH){\cdot}CH_2{\cdot}CO \\ | \qquad\qquad / \\ CH_2{\cdot}NMe_3{\cdot}O \end{array}$$

β-Hydroxy-γ-butyrotrimethylbetaine was synthesised by Rollett (*ibid.* 1910, **69**, 60), Tomita (*ibid.* 1923, **124**, 253), and Engeland (Ber. 1910, **43**, 2705) and said not to be identical with carnitine. α-*Hydroxy-γ-butyrotrimethylbetaine*, synthesised by Fischer and Göddertz (*ibid.* 1910, **43**, 3272), also differs from carnitine. This synthesis was questioned by Engeland (*ibid.* 1921, **54**, 2208) but a new synthesis by Crawford and Kenyon (J.C.S. 1927, 396) who showed that this betaine gave carbon monoxide on heating with sulphuric acid and not *apo*carnitine, upheld the contention of Fischer and Göddertz that carnitine is not the α-hydroxy compound. Fresh evidence presented by Tomita and Sendju (Z. physiol. Chem. 1927, **169**, 263) suggests that carnitine is actually the β-hydroxybetaine. They resolved *γ-amino-β-hydroxybutyric* acid into its two optical isomers (four isomers were actually claimed, two being subsequently proved by Bergmann and Lissizyn (Ber. 1930, **63**, 310) to be partial racemates). Exhaustive methylation of the *l*-acid gave a betaine with properties in complete agreement with those of natural *l*-carnitine. The failure reported for the previous syntheses of the β-hydroxybetaine was presumably due to the difference in the properties of *l*- and *r*-carnitine.

Acetylcarnitine.—This base, formed by cold acetylation of carnitine, has m.p. 145° ; hydrochloride, m.p. 181° ; chloroaurate, m.p. 128° ; chloroplatinate, m.p. 187° (Krimberg and Wittandt, Biochem. Z. 1931, **251**, 229).

***apo*Carnitine or Crotonbetaine.**—This unsaturated betaine is formed by heating carnitine with sulphuric acid (*see above*) and has also been isolated from the lysine fraction of the bases of Liebig's meat extract by Linneweh who has identified it by synthesis as γ-crotonotrimethylbetaine,

$$\begin{array}{lr} CH{:}CH & \text{—}CO \\ | & | \\ CH_2{\cdot}NMe_3 & {\cdot}O \end{array}$$

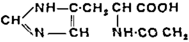
and proposed the name "crotonbetaine" for the base (Z. physiol. Chem. 1928, **175**, 91 ; **176**, 217). The *chloroaurate* melts at 215°–217°, and the *ethyl ester chloroplatinate* at 223°–225°.

It is, perhaps, of interest that the saturated betaine, **γ-butyrotrimethylbetaine**, has also been obtained from natural sources (Brieger,

"Untersuchungen uber Ptomaine," III, Hirschwald, Berlin, 1886, Takeda, Pflüger's Archiv. 1910, 133, 365; Engeland and Kutscher, Z physiol Chem 1910, 69, 282; Ackermann, Z. Biol 1927, 86, 199). It was called *actinine* by Ackermann, who isolated it from *Actinia equina*

The properties of the three bases carnitine, crotonbetaine, and γ butyrobetaine have been compared by Linneweh (Z. physiol. Chem. 1929, 181, 42, 54; 182, 8) W. V. T.

CARNOSINE. *a (β-alanyl)amino β-iminazolyl propionic acid*,



This base was first isolated from Liebig's extract of beef and has since been obtained in varying amount from the muscles of many different species including cat, dog, deer, gnu, horse, opossum, ox, rabbit, crocodile, river eel and boa constrictor. It is not present in the muscles of the llama, crow, goose, hen, pigeon, turkey, cod, conger eel and dog fish, which contain *N* methylcarnosine, *anserine* (*q v*) (Smorodinzew, Z. physiol Chem. 1913, 87, 20, 1914, 92, 19, 227; Ackermann, Timpe and Poller, *ibid* 1929, 183, 1; Hoppe Seyler, Linneweh and Linneweh, *ibid*. 184, 276, Ackermann and Hoppe-Seyler, *ibid*. 1931, 197, 135; Wolff and Wilson, J. Biol Chem. 1932, 95, 495; 1935, 109, 565; Kapeller-Adler and Haas, Biochem. Z. 1934, 269, 263).

Carnosine is soluble in water, crystallises in rosettes of large colourless needles, m p. 246°–250° (decomp). It has $[\alpha]_D +21°$ independently of the concentration (Gulewitsch, Z. physiol. Chem. 1913, 87, 6), and has a strongly alkaline reaction. The vapours of carnosine give the pyrrole reaction with a pine splinter (Gulewitsch, *ibid*. 8) Carnosine may be precipitated from an aqueous extract of muscle by a saturated solution of mercuric sulphate in 5% sulphuric acid; the precipitation is accelerated by the addition of 2 vols. of alcohol and a little ether (Dietrich, Z. physiol. Chem. 1914, 92, 212). Smorodinzew (*ibid* 214) recommends a 10% solution of mercuric sulphate in 5% sulphuric acid solution. Carnosine can be isolated by precipitation with a copper salt as the *derivative* $C_9H_{14}N_4O_3\,CuO$, which is crystalline, very sparingly soluble in water, has a distinctive blue colour, and decomposes without melting at 220° (Mauthner, Monatsh 1913, 34, 883). It is not obtained in the presence of nitric acid (*e g*. from carnosine nitrate and copper carbonate), a copper compound containing nitric acid being formed This compound is very soluble in water, from which it will not crystallise, insoluble in alcohol, and has not the distinctive blue colour of the carnosine copper compound (Dudley and Thorpe, *unpublished*). The *nitrate*, $B\,HNO_3$, crystallises in large stellate clusters of needles, m p. 219° (decomp.), $[\alpha]_D^{19\cdot3}$ +22 2°, $c = 7\,820$°. The rotatory power increases slightly on dilution, it falls to about half its value in presence of nitric acid (Gulewitsch, Z physiol. Chem. 1913, 87, 1). The *silver* derivative and acid double salt with silver nitrate closely resemble the corresponding derivatives of arginine (Gulewitsch and Amiradžibi, Ber. 1900, 33, 1902).

The *monoflavianate* crystallises with $3H_2O$ and melts (anhyd.) at 110° (Langley and Albrecht, J. Biol. Chem. 1935, 108, 729). The following derivatives and their melting-points are given by Smorodinzew, J.C S 1923, 124, i, 593); *sulphate*, 238°–240°; *orthophosphate*, 205°–207°; *metaphosphate*, 200°–203°; *iodate*, 188°–190°; *oxalate*, 216°–218°; *tartrate*, 195°–200°; *phenylcarbamido derivative*, 178°–180°.

Carnosine is probably identical with Kutscher's *ignotine* (Z. Nahr. Genussm. 1905, 10, 528; Gulewitsch, Z. physiol. Chem. 1906 50, 204; 1907, 51, 258; 52, 527). Compare, however, Kutscher (*ibid*. 1906, 50, 445; 1907, 51, 545).

When carnosine is hydrolysed by boiling with barium hydroxide it yields histidine and β alanine. That carnosine is β-alanylhistidine is shown by its synthesis from histidine and β iodopropionyl chloride (Bauman and Ingvaldsen, J. Biol. Chem. 1918, 35, 263). This is further proved by its behaviour towards 2 4 5-trinitrotoluene (Barger and Tutin, Biochem J. 1918, 12, 402). It has been synthesised by condensing β-nitropropionyl chloride with histidine methyl ester and reducing the resulting products with stannous chloride and hydrochloric acid (*idem ibid*). More recently Sifferd and Du Vigneaud (J. Biol Chem 1935, 108, 753) have synthesised carnosine in 65% yield from *l* histidine and carbobenzyloxy-β alanine

The enantiomorph of natural carnosine, *d-carnosine*, has been prepared by a similar method from *d* histidine by Du Vigneaud and Hunt (*ibid*. 1936, 115, 93). It has $[\alpha]_D^{20}$ −20 4° in water and melts at 260°.

The carnosine content of flesh extracts may be estimated by two colorimetric methods which control one another; the one depends on the colour yielded by the histidine complex in the carnosine molecule with diazobenzene-sulphonic acid (Weiss and Sobolev, Biochem Z. 1913, 58, 119); the other on the violet colour yielded by carnosine when boiled with cupric hydroxide, Fürth and Hryntschak (*ibid*. 1914, 64, 172). The determination of carnosine by the two colour methods is stated by Kuen (*ibid*. 1927, 189, 60) to give high results compared with methods involving the isolation of the carnosine copper compound. Clifford and Mottram (Biochem. J. 1928, 22, 1246) still maintain that the diazo method is reliable It cannot, however, be regarded as specific since other substances such as anserine and histidine give the reaction. For the determination of carnosine in the presence of these substances, see Kapeller-Adler and Haas (Biochem. Z. 1934, 269, 263). M. A. W. and W. V. T.

CARNOTITE. A hydrated vanadate of uranium and potassium, occurring abundantly as a bright canary yellow powder disseminated in sandstone in western Colorado. C. Friedel and E. Cumenge (Compt. rend. 1899, 128, 532), by whom it was first described and named (after A. Carnot), expressed the composition by the formula $K_2O{\cdot}2U_2O_3{\cdot}V_2O_5,3H_2O$. Detailed analyses were made by W. F. Hillebrand (Amer. J. Sci. 1900, 10, 120), and he concluded that the

mineral is not simple, but a mixture. This view is, however, not borne out by T. Crook and G. S. Blake (Min. Mag. 1910, 15, 271), who find that the material, both from Colorado and from South Australia, is definitely crystallised as minute plates possessing orthorhombic symmetry and with characters analogous to those of autunite. F. L. Hess and W. F. Foshag (Proc. U.S. Nat. Mus. 1927, 72, no. 12) from an analysis of crystalline material from Utah give the formula $3(K_2O \cdot 2UO_3 \cdot V_2O_5),2H_2O$.

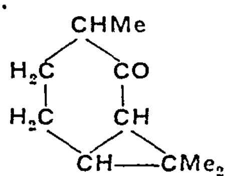
The carnotite-bearing sandstones occur over an extensive tract of country on both sides of the Colorado-Utah boundary, the richest deposits being in the neighbourhood of La Sal Creek, Roc Creek, and Paradox Valley, in Montrose Co., and in San Miguel and Dolores Cos., in south-west Colorado ; other deposits are met with near Coal Creek in Rio Blanco Co. and Skull Creek in Routt Co. in north-west Colorado, and at Mauch Chunk, Pennsylvania. Most of these deposits are in Jurassic (La Plata) sandstone, but some of those in the N.W. are in sandstones of Cretaceous age. They have been mined at several spots, and a plant for the extraction of uranium, radium and vanadium salts was erected near Cedar in San Miguel Co., Colorado ; but the sandstone ore is of a low grade, and the difficulties of transport are considerable. An average sample of marketed ore assayed U_3O_8 11·49% and V_2O_5 6·40% (R. B. Moore and K. L. Kithil, Bull. U.S. Bureau of Mines, 1913, 70 ; C. L. Parsons and others, *ibid.* 1915, 104).

In South Australia, at Radium Hill, near Olary, carnotite occurs as films on the joint-planes of a large deposit of ilmenite, rutile, and magnetite.

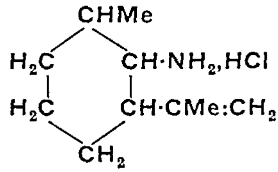
A closely allied mineral, named *ferganite* (I. A. Antipov, 1908 ; Abstr. in Jahrb. Min. 1909, ii, 38), is a hydrated vanadate of uranium with some lithium. It occurs, together with other uranium minerals, in prov. Fergana in Russian Turkestan. L. J. S.

CAROB TREE. Locust tree (*Ceratonia siliqua*, Fam. Leguminosæ). Widely cultivated in Mediterranean countries. The pods (carobs) are a food for men and animals, and a syrup and also alcohol are prepared from them in Sicily. The pods are generally known as St. John's bread, from a misinterpretation of St. Matthew, III, 4. The fruits (without seed) contain up to 30% sugar, the peel 29–34% saccharose and 8·5–11% reducing sugars, but the proportions vary considerably: The seeds contain mannan and *d*-mannose, formerly described as *caroubin* and *caroubinose* respectively (Alberda van Ekenstein, Compt. rend. 1897, 125, 719).

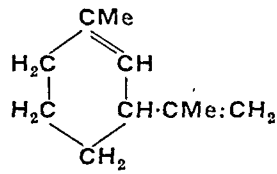
CARONE.



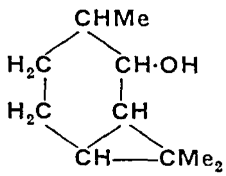
The dicyclic ketone, *carone*, $C_{10}H_{16}O$, b.p. 98°/13 mm., d_4^{17} 0·955, n_D^{16} 1·478, $[\alpha]_D$ +134°, does not occur in nature and was first prepared by Baeyer (Ber. 1894, 27, 1919) by the action of alcoholic potassium hydroxide on dihydrocarvone hydrobromide. It can be characterised by the preparation of its *semicarbazone*, m.p. 167°–169°, or its *bisnitroso-* derivative, m.p. 116°–118°. The *oxime* of *d*-carone is an oil, b.p. 130°–132°/12 mm., whilst that prepared from *dl*-carone has m.p. 77°–79°. On reduction with sodium and alcohol the oxime yields the dicyclic base d-*carylamine*, b.p. 88°–89°/15 mm., $[\alpha]_D$ +72·3° (in alcohol) (Baeyer, Ber. 1894, 27, 3486), the hydrochloride of which is readily isomerised to *vestrylamine hydrochloride* (I) from which *carvestrene* (II) can readily be prepared. By treatment of carylamine sulphate with nitrous acid the secondary alcohol,



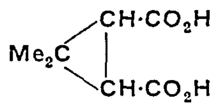
I.



II.



III.



IV.

carol (III), b.p. 141°–142°/100 mm., d_{30}^{30} 0·9181, n_D^{30} 1·472, $[\alpha]_D$ −42·92°, is obtained (Menon and Simonsen, J. Indian [Inst. Sci. 1927, 10, A, 7). This alcohol cannot be prepared by the direct hydrogenation of the ketone, fission of the *cyclo*propane ring occurring (Iyer and Simonsen, J.C.S. 1926, 2049). On oxidation with potassium permanganate carone yields a mixture of cis- and trans- *caronic acids* (IV) (Baeyer, Ber. 1896, 29, 2747), which have been synthesised by Perkin and Thorpe (J.C.S. 1898, 75, 48). J. L. S.

CARO'S ACID. Anhydropermonosulphuric acid, $O(SO_2 \cdot O \cdot OH)_2$.

CAROTENE. The isolation of carotene was first effected by Wackenroder in 1831, who obtained the crystalline pigment from the root of the carrot. In 1847 Zeise obtained it in quantity sufficient for elementary analysis and proved it to be a hydrocarbon of the empirical formula C_5H_8, but it was not until 1907 that Willstätter and Mieg (Annalen, 1907, 355, 1) ascribed to it the true molecular formula $C_{40}H_{56}$.

Carotene is widely distributed throughout both the plant and animal kingdoms, its

presence in the latter being presumably related to its ingestion in the food. The carotene content of various plant products is illustrated by the following data: 1 g. of pigment is obtained from 1 kg. dry carrots (Escher, "Zur Kenntniss des Carotins und des Lycopins," Zürich, 1909), 0 15–0 20 g. from 1 kg. of stinging nettles (Willstätter and Stoll "Untersuchungen über Chlorophyll," Berlin, 1913), 0 3 g. from 1 kg. dry paprika (*Capsicum annuum*) (Zechmeister and Cholnoky, Annalen, 1927, 455, 20), and 0 3–0 6 g. from 1 kg of green leaves of various types, whilst the richest source appears to be the green alga *Trentepohlia iolithus* (Tischer, Z. physiol. Chem. 1936, 243, 103) which contains 0 3% carotene. The carotene contents of many animal products, for example, of cow and of goat butter (Gillam and Heilbron, Biochem. J. 1933, 27, 878), of fish liver oils (Schmidt Nielsen, Sörensen, and Trumpy, Norske Vidensk. Selsk. 1932, 5, 114, 118), and of fish roe (von Euler, Gard and Hellström, Svensk Kem Tidskr. 1932, 44, 191) have been examined Zechmeister finds that the ratio $\frac{\text{lipochrome}}{\text{lipoid}}$ is between $\frac{1}{100,000}$ and $\frac{1}{300,000}$; thus 6 mg of carotene are obtained from 2 kg of horse fat and 11 mg from 1 kg. of cow fat.

Crystalline carotene is readily obtainable in quantity from carrots (*Daucus carota*), stinging nettle (*Urtica*), the berries of the mountain ash (*Sorbus Aucuparia*), the giant pumpkin (*Cucurbita maxima*), and from palm oil. A typical method of isolation of the pigment is given by Willstätter and Escher (Z. physiol. Chem. 1910, 64, 47) in which dried and minced carrots are extracted by percolation with light petroleum. Carbon disulphide is added to the concentrated extract and the carotene precipitated by the addition of alcohol. Carotene obtained by this and similar methods separates in deep reddish-violet plates, m p 172°–174°, moderately soluble in most organic solvents with the exception of alcohol. Such preparations exhibit absorption maxima at 524–510, 490–475$m\mu$ in carbon disulphide; the concentration of a carotene solution can be estimated from the intensity of absorption. For a rapid assay of carotene solutions, however, simpler methods are available which depend upon matching the colour of a carotene solution against a known standard. Willstätter and Stoll ("Untersuchungen über Chlorophyll," Berlin, 1913) used 0 2% aqueous potassium dichromate which in a layer 100 mm. thick is equivalent to a similar layer of a carotene solution containing 0 0268 g in 1 litre of light petroleum Kuhn and Brockmann (Z. physiol. Chem. 1932, 206, 41) have found that an alcoholic solution of azobenzene gives a better comparison; a solution of 14 5 mg. azobenzene in 100 c c. 95% alcohol is colorimetrically equivalent to one containing 0 235 mg. carotene in 100 c.c. light petroleum.

Carotene oxidises rapidly on exposure to air either in the solid state or in solution. In the case of crystalline carotene Willstätter and Escher (*l c.*) observed an oxygen intake of 0 3% after 5 days, and finally after several months of 35% corresponding to 11–12 oxygen atoms, to give a white amorphous product. Baumann and Steenbock (J. Biol. Chem 1933 101, 561) have shown that the degree of autoxidation of solutions of carotene in oil is markedly smaller.

Heterogeneity of Plant Carotene.—Whilst it had been frequently observed that carotene preparations from different plant sources had different melting points it was not until 1931 that Kuhn and Lederer (Ber. 1931, 64, [B], 1349; Cf. Karrer, Helfenstein, Wehrli, Pieper and Morf Helv. Chim. Acta, 1931, 14, 614) showed that the pigment exists in isomeric forms. By chromatographic resolution of crystalline carotene (*see* CAROTENOIDS) an optically active isomer, α-carotene, was isolated together with the optically inactive β carotene. Subsequently minute amounts (0 1% of total carotene) of a third isomer, γ carotene, were detected by application of the chromatographic method (Kuhn and Brockmann, Ber. 1933, 66, [B], 407) It has been established that the β isomer invariably predominates from whatever source the carotene mixture is obtained; the percentage of α-carotene in the gross carotene fractions from various sources is as follows palm oil, 30–40%; chestnut leaves, 25%, carrots, 10–20%; mountain ash berries, 15%, melon, 1%; whilst various grasses, spinach, and nettles contain but traces.

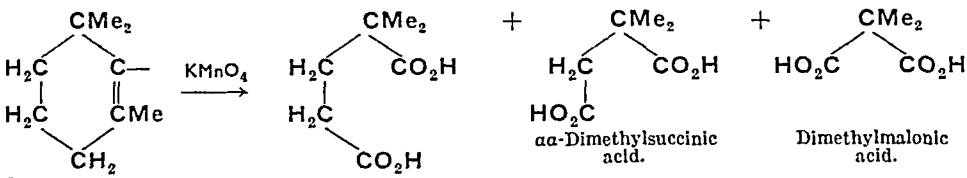
β Carotene.—β Carotene, $C_{40}H_{56}$, crystallises from a mixture of benzene and methyl alcohol in which it is less soluble than the α isomer, in deep red plates with a violet reflex, m p. 183°; it is optically inactive and exhibits absorption maxima at 514, 484 (ϵ=150,000) and 447$m\mu$ in carbon disulphide. With the antimony trichloride reagent it gives a blue colour which has an absorption maximum at 590$m\mu$ (α carotene exhibits a maximum under similar conditions at 542$m\mu$, this difference being of great assistance in identification). With iodine it gives a di iodide of indefinite melting-point from which an isomeric *iso*carotene is regenerated, on removal of the halogen

The importance of β carotene in the economy of life lies in the fact that it can replace the vitamin A of liver oils, being converted into the latter in the animal organism (*see* CAROTENOIDS)

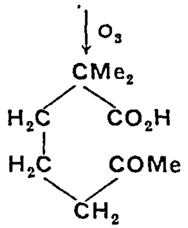
Although several of the degradations which have led to the establishment of the structure of β-carotene were carried out on material which was subsequently shown to be a mixture, the evidence obtained therefrom is effective because it has been established that β carotene was the preponderating component of the mixture employed.

β-Carotene contains 11 ethylenic linkages (Zechmeister, Cholnoky and Vrabély, Ber. 1928, 61, [B], 566; 1933, 66, [B], 123), and is therefore dicyclic; the presence of 6 extra-chain methyl groups of the type =CMe— was established by drastic chromic acid oxidation (Kuhn and L'Orsa, Z. angew. Chem. 1931, 44, 847; Kuhn and Roth, Ber. 1933, 66, [B], 1274). The identification of the fragments obtained by oxidation of carotene with potassium permanganate and with ozone has been of great value in the structural study of the pigment. Oxidation of a

solution of carotene (mainly the β-isomer) in benzene solution with cold aqueous potassium permanganate gives αα-dimethylglutaric acid, αα-dimethylsuccinic acid, and dimethylmalonic acid (Karrer and Helfenstein, Helv. Chim. Acta, 1929, 12, 1142) whilst ozonolysis of the pigment yields geronic cid (Karrer, Helfenstein, Wehrli and Wettstein, *ibid.* 1930, 13, 1084). The identification of these degradation products *clearly indicates the presence of at least one β-ionone ring system.* A repetition of the ozonolysis experiment using pure β-carotene showed that 16% of the calculated yield of geronic acid was obtained assuming that *β-carotene contains two β-ionone ring systems.* At the same time, it was ascertained that β-ionone itself gives 19·4% of geronic acid under similar conditions (Karrer and Morf, *ibid.* 1931, 14, 1033), and hence the presence of two β-ionone rings in β-carotene was established.



β-Ionone fragment. αα-Dimethylglutaric acid. αα-Dimethylsuccinic acid. Dimethylmalonic acid.



Geronic acid.

From this data the symmetrical structure for β-carotene (I), p. 396, was postulated, the detailed structure of the polyene chain, in so far as the location of the methyl group attachments is concerned, being mainly based upon a high degree of probability.

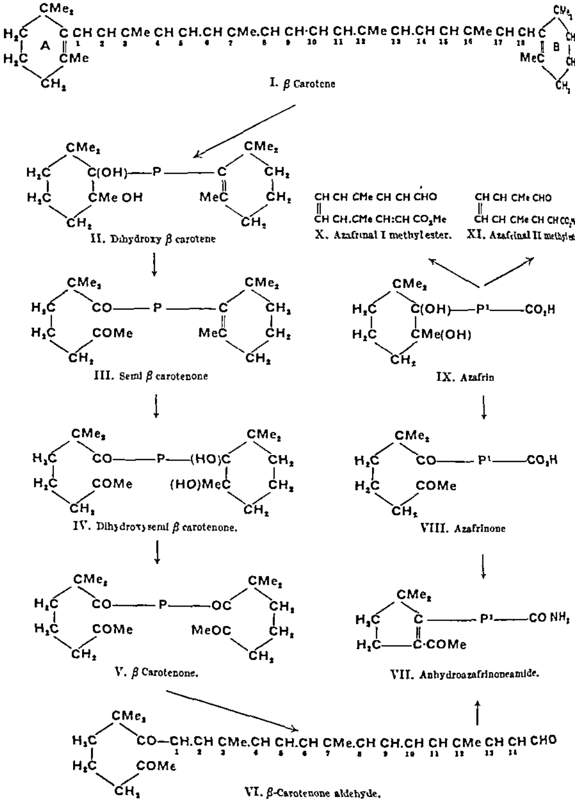
The symmetrical structure (I) has recently been confirmed by Kuhn and Brockmann (Annalen, 1935, 516, 95) by means of an elegant series of degradation experiments. Mild oxidation of β-carotene with chromic acid gives a dihydroxy-β-carotene (II) the constitution of which is established by its oxidation with the Criegee reagent to semi-β-carotenone (III). Controlled oxidation of either dihydroxy-β-carotene or of semi-β-carotenone with chromic acid gives β-carotenone (V), also obtained by the direct oxidation of β-carotene. An intermediate in the oxidation of semi-β-carotenone to β-carotenone has been isolated by the mild chromic acid oxidation of dihydroxy-β-carotene; this is formulated as a dihydroxysemi-β-carotenone (IV), since on oxidation with lead tetra-acetate it gives β-carotenone.

Further oxidation of either β-carotenone, dihydroxysemi-β-carotenone, semi-β-carotenone, or of dihydroxy-β-carotene with chromic acid gives β-carotenone aldehyde, $C_{27}H_{36}O_3$ (VI), which is also obtained by the direct oxidation of β-carotene. The identity and symmetrical distribution of the two ring systems of β-carotene is satisfactorily confirmed by the non-occurrence of isomerides of the first four oxidation products (II, III, IV, V) of the pigment, and by the establishment of the function of the oxygen atoms present therein, whilst the complete symmetry of the polyene chain of the hydrocarbon follows from the fact that one and only one β-carotenone aldehyde is obtained from the hydrocarbon and its first four oxidation products.

β-Carotenone aldehyde gives 4 mols. of acetic acid on drastic oxidation, from which it follows that its polyene chain carries three methyl group attachments, 1 mol. of acetic acid being ascribed to the terminal acetyl group. Without making an assumption regarding the location of the methyl group attachments in the polyene chain, it is clear that the formation of β-carotenone aldehyde from either β-carotene or β-carotenone is effected by chain fission between C_3 and C_4 (or between C_{15} and C_{16}). Since β-carotenone aldehyde contains only three methyl group attachments in the polyene chain it follows that one of the four β-carotene extra-chain methyl groups is attached between the β-ionone ring A and C_4 and another between the β-ionone ring B and C_{15}.

β-Carotenone aldehyde gives a dioxime with excess and a monoxime with 1 mol. of hydroxylamine; the latter is a mixture of ketoxime and aldoxime and gives on dehydration a mixture of unchanged ketoxime and a nitrile which are separable chromatographically. Controlled hydrolysis of this nitrile gives an amide (VII), which is identical with anhydroazafrinoneamide prepared from azafrinone (VIII) by successive treatment with thionyl chloride and ammonia, followed by cyclisation of the 1:6-diketone system with alkali. β-Carotenone aldehyde is thus the aldehyde of azafrinone and the polyene chain of azafrin (IX) must be identical with part of that of β-carotene; evidence concerning the polyene chain of azafrin can now be directly applied to that of β-carotene.

Oxidation of the methyl ester of azafrin gives a mixture of two aldehyde esters, azafrinal-I methyl ester (X), $C_{15}H_{18}O_3$, and azafrinal-II methyl ester (XI), $C_{13}H_{16}O_3$, both of which contain two extra-chain methyl groups. The formation of the former is consequent upon rupture of the azafrin polyene chain between C_3 and C_4, and of the latter upon rupture between C_5 and C_6. Since both aldehydes contain only two extra-chain methyl groups, the third extra-chain methyl group of azafrin must be located between the ring and C_4, a conclusion in harmony with that arrived at from



I. β Carotene

II. Dihydroxy β carotene

III. Semi β carotenone

IV. Dihydroxysemi β carotenone.

V. β Carotenone.

VI. β-Carotenone aldehyde.

VII. Anhydroazafrinoneamide.

VIII. Azafrinone

IX. Azafrin

X. Azafrinal I methyl ester.

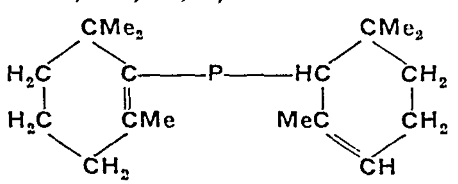
XI. Azafrinal II methyl ester

P = the polyene chain (C_1—C_{18}) in β carotene.

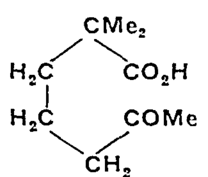
P¹ = the polyene chain (C_1—C_{14}) in β carotenone aldehyde.

a consideration of β-carotenone aldehyde. Furthermore, since azafrinal-II is an aldehyde, a methyl group cannot be attached to C_6, so both methyl groups of the azafrinals-I and -II must be attached between C_7 and C_{14}. Thermal decomposition of azafrin gives *m*-toluic acid, *m*-xylene, and toluene, from which it is clear that a methyl group must be attached at either C_{10} or C_{12}, a conclusion necessitating a symmetrically attached methyl group at either C_9 or C_7 respectively; *i.e.* the polyene chain of azafrin has methyl group attachments at either C_9 and C_{10} or C_7 and C_{12}. The former arrangement, however, does not allow of the interpretation of the formation of *m*-xylene by thermal decomposition of azafrin ; consequently methyl groups must be attached to C_{12} and C_7. The formation of *m*-xylene from azafrin now requires that the third methyl group of its polyene chain is attached to C_3. The symmetrical nature of the β-carotene chain locates the remaining extra-chain methyl group at C_{16}; therefore the polyene chain of β-carotene carries methyl group attachments at C_3, C_7, C_{12}, and C_{16}, and the symmetrical structure (I) for β-carotene is experimentally confirmed.

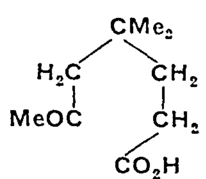
α-Carotene, $C_{40}H_{56}$, crystallises from a mixture of benzene and methyl alcohol in deep red prisms, m.p. 187°–188°, $[\alpha]^{18}_{6438}$ +385° (in benzene); absorption maxima 507, 478 (ϵ= 130,000), and 446$m\mu$ in carbon disulphide. With antimony trichloride in chloroform solution it gives a blue solution exhibiting an absorption maximum at 542$m\mu$. Ozonisation of α-carotene yields *iso*geronic acid, in addition to geronic acid, and as the optical activity indicates asymmetry Karrer proposed the structure (XII) for the pigment (Helv. Chim. Acta, 1933, 16, 975). α-Carotene can replace vitamin A in the diet of animals ; in consequence of the fact that it contains only one β-ionone fragment, its physiological activity is only half that of β-carotene (Kuhn and Brockmann, Annalen, 1935, 516, 95).



XII. α-Carotene.



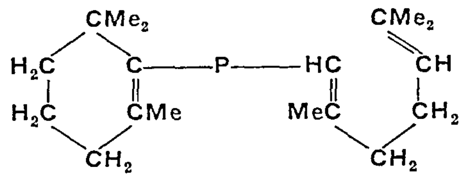
Geronic acid.



*iso*Geronic acid.

Various oxidation products of α-carotene have been described (Karrer, Solmssen and Walker, Helv. Chim. Acta, 1934, 17, 417; Karrer, von Euler, and Solmssen, *ibid.* 1934, 17, 1169).

γ-Carotene, $C_{40}H_{56}$, crystallises from a mixture of benzene and methyl alcohol in deep red prisms with a blue reflex. It exhibits absorption maxima at 533, 496, and 463$m\mu$ in carbon disulphide. Kuhn and Brockmann (Ber. 1933, 66, [B], 407) showed that γ-carotene absorbs 12 mols. of hydrogen on catalytic hydrogenation, and that ozonolysis yielded 1 mol. of acetone and 1 mol. of geronic acid, from which data they have proposed the monocyclic structure (XIII):



XIII. γ-Carotene.

This formulation is supported by the physiological activity of the pigment, which is equal to that of α-carotene.

isoCarotene or δ-carotene, $C_{40}H_{56}$, does not appear to exist in nature. It is prepared by the decomposition of β-carotene di-iodide, with sodium thiosulphate and forms violet crystals, m.p. 180°–181°, from a mixture of benzene and methyl alcohol (Kuhn and Lederer, Ber. 1932, 65, [B], 637). Karrer, Schöpp, and Morf (Helv. Chim. Acta, 1932, 15, 1158), however, give m.p. 192°–193° for *iso*carotene; they report that it contains 12 ethenoid linkages, and that ozone gives neither geronic nor *iso*geronic acids, indicating the absence of both the α- and the β-ionone ring systems.

pseudo-α-Carotene.—By repeated chromatographic adsorption on alumina, β-carotene is isomerised to *pseudo*-α-carotene, m.p. 166°, which on re-adsorption is partially reconverted into β-carotene; *pseudo*-α-carotene is spectroscopically identical with α-carotene, but differs from it in being optically inactive. Catalytic hydrogenation indicates that the new isomeride contains eleven ethenoid linkages, absorption spectra data showing that only ten of these are conjugated (Gillam and El Ridi, Biochem. J. 1936, 30, 1735).

I. M. H., R. F. P., and F. S. S.

CAROTENOIDS (lipochromes, polyene pigments ; *see also under* individual pigments, Algæ, and Vitamin A). The carotenoids comprise a class of bright yellow to violet pigments widely distributed in both the vegetable and animal kingdoms. They are insoluble in water but freely soluble in the usual lipoid solvents (hence the alternative name lipochromes). Further, they are characterised by their sensitivity to oxygen, by which they are bleached, by the blue colours which they give with concentrated sulphuric acid, and by their well-defined absorption spectra. They are either hydrocarbons or oxygenated derivatives thereof ; no naturally occurring carotenoids are known which contain other elements. The name carotenoid is derived from the orange-yellow pigment carotene first obtained from the carrot (*Daucus carota*) by Wackenroder in 1831 (*cf.* Tswett, Ber. deut. bot. Ges., 1911, 29, 630).

The first investigations of chemical significance are due to Willstätter and his collaborators, who

during the years 1906–1914 isolated several of the more common carotenoids in crystalline form and established their empirical formulæ. Thus Willstätter and Mieg (Annalen, 1907, 355, 1) showed that carotene is a hydrocarbon, $C_{40}H_{56}$, and demonstrated that it also accompanies chlorophyll in green leaves. Willstätter and Escher (Z physiol. Chem. 1910, 64, 47) showed that lycopene, the pigment previously isolated from the ripe tomato by Millardet, is an isomer of carotene. An oxygenated member of the series, leaf xanthophyll, $C_{40}H_{56}O_2$, was isolated by Willstätter and Mieg (l c.) who found that it accompanies chlorophyll and carotene in leaf foliage. The yellow lipochrome of egg yolk, lutein, $C_{40}H_{56}O_2$, was shown to be closely related to, if not identical with, leaf xanthophyll (Willstätter and Escher, Z physiol Chem. 1912, 76, 214).

Of other pigments described at this period, mention may be made of fucoxanthin, $C_{40}H_{56}O_6$, obtained from *Fucus vesiculosus*, a member of the brown algæ (Willstätter and Page, Annalen, 1914, 404, 237; for a complete review, *see* Willstätter and Stoll, "Untersuchungen über Chlorophyll," Berlin, 1913; and "Untersuchungen über Assimilation der Kohlensäure," Berlin, 1918).

The rational development of the chemistry of the carotenoid pigments after this preliminary period of isolation and characterisation was made possible by the introduction of the method of quantitative catalytic hydrogenation; by this method. Karrer and Widmer (Helv. Chim. Acta, 1928, 11, 751) found that lycopene absorbs 13 mols. of hydrogen yielding a paraffin hydro carbon, $C_{40}H_{82}$, from which it follows that lycopene must be acyclic. In the same way, Kuhn, Winterstein and Kaufmann found that lutein is dicyclic (Ber 1930, 63, [B], 1489). The more important of the subsequent investigations which led to the elucidation of the structure of the carotenoids include, on the one hand, a study of the synthetic diphenylpolyenes (Kuhn and Winterstein, Helv. Chim Acta, 1928, 11, 87, 427, 1929, 12, 899) which effected a correlation of colour with the degree of conjugation, and on the other, the oxidation (ozone and potassium permanganate) experiments of Karrer, to which more specific reference will be made later.

Contemporaneously, a method was being refashioned and applied to the study of carotenoids which was to exert a profound influence upon the future development of the subject. In 1906 Tswett observed that when a solution of a carotenoid mixture in a non-polar solvent is filtered through a column of an adsorbent such as calcium carbonate, the components of the mixture orient themselves as separate coloured zones easily identified on the white adsorbent. The definition and individuality of the zones is increased by continued washing with the pure solvent ("development of the chromatogram"), after which they are separated mechanically and the pigments extracted from the adsorbent. In addition to its value as a means of resolution of carotenoid mixtures the method also provides constitutional information in so far as it is established that hydroxylated carotenoids are considerably more strongly adsorbed than are the hydrocarbon pigments, and secondly that the location of the pigmented zones upon the chromatogram is dependent upon the magnitude of both the total and conjugated unsaturation of the different pigments.

The most useful adsorbents for chromatographic resolution of carotenoid pigments are alumina, calcium hydroxide, calcium carbonate, and magnesia. After the mechanical separation of the coloured zone of the developed chromatogram, the pigment is isolated by extraction with methyl alcohol, and a further purification effected by a repetition of the process with each of the components A final purification is achieved by crystallisation. A complete account of the varying techniques and applications of chromatography is to be found in the monograph by Zechmeister and Cholnoky, "Die Chromatographische Adsorptionsmethode," Vienna, 1937. The variation in the tenacity with which a group of carotenoids is held by adsorbents is illustrated in Table I (Winterstein, "Klein's Handbuch der Pflanzenanalyse," Vienna, 1933, II, 1403). It is to be noted that in the case of the xanthophylls, the more heavily oxygenated the pigment, the more strongly is it adsorbed, whilst hydrocarbons are relatively weakly adsorbed. In this respect, completely esterified xanthophylls are intermediate between the hydrocarbons and the xanthophylls.

TABLE I.

Solvent	*Light petroleum.*		*Adsorbing media*
More strongly adsorbed	Fucoxanthin Violaxanthin Taraxanthin Flavoxanthin Zeaxanthin Lutein	Alcohols	Calcium Carbonate
	Physalien Helenien	Esters	
Less strongly adsorbed	Lycopene γ-Carotene β Carotene α Carotene	Hydrocarbons	Alumina

A preliminary partial separation of the components of a carotenoid mixture is often possible by partition between two non-miscible solvents Thus, when a mixture of pigments is shaken with light petroleum and 80–90% methyl alcohol, the hydrocarbons and esters in general partition into the light petroleum phase (epiphasic pigments) whilst more strongly hydroxylated components pass preferentially into the alcohol (hypophasic pigments). The method is illustrated by the appended scheme (Table II) for the separation of a mixture of α- and β carotenes, lycopene, lutein and its esters, zeaxanthin and its esters, violaxanthin and its esters, crocetin, and chlorophyll (Kuhn and Brockmann, Z physiol. Chem. 1932, 206, 41).

The methods which are briefly sketched in Table II have for the most part been of inestimable service in the isolation and purification of carotenoid pigments. The study of the light absorption properties of the carotenoids, on the other hand, has been of more fundamental value in the constitutional study of these pigments. In by far the greater number of the carotenoids the chromophoric group responsible

TABLE II.—MIXTURE PARTITIONED BETWEEN LIGHT PETROLEUM AND 90% METHANOL.

Light petroleum phase.		*Methanol phase.*	
α- and β-Carotenes, lycopene, xanthophyll-esters and chlorophyll. Saponified and repartitioned between light petroleum and 90% methanol.		Free lutein, zeaxanthin, violaxanthin, crocetin, and chlorophyll (traces). Mixture saponified, diluted with an equal volume of water and again extracted with light petroleum.	
Light petroleum.	*Alcohol.*	*Light petroleum.*	*Alcoholic-aqueous alkali.*
α- and β-Carotenes Lycopene.	Diluted and extracted with light petroleum : Lutein Zeaxanthin, Violaxanthin.	Lutein. Zeaxanthin Violaxanthin.	Chlorophyll and crocetin. Acidify and extract with light petroleum : Crocetin.

for the selective absorption of light and consequently for the colour is the conjugated polyene chain. It is well established that an increase in the number of conjugated linkages is accompanied by a displacement of the absorption maxima towards the red end of the spectrum. Conversely, a knowledge of the location of the absorption maxima of a carotenoid allows of a prediction of the nature of the chromophoric group. It is not possible in this review to recount the various rôles played by spectroscopy in carotenoid chemistry ; it must suffice to quote the absorption maxima of a series of carotenoids and their derivatives (Table III) in which the effect of alteration of the chromophore upon the location of these maxima is apparent.

TABLE III.

Chromophore.*	Carotenoid.	Optical maxima (in carbon disulphide).
10 ⊧ + C:O	Lycopenal [1]	569, 528·5, 493·5.
11 ⊧	Lycopene [2]	548, 507·5, 477.
⊧′ + 9 ⊧ + C:O	Capsanthin [3]	543, 503·5.
⊧′ + 9 ⊧ + C:O	Semi-β-carotenone [4]	538, 499.
C:O + 9 ⊧ + C:O	β-carotenone [5]	538, 499, 466.
C:O + 9 ⊧ + C:O	Capsorubin [3]	541·5, 503, 468.
C:O + 9 ⊧ + C:O	Bixin dialdehyde [2]	539·5, 502, 467·5.
9 ⊧ + C:O	Semi-α-carotenone [6]	533, 499.
⊧′ + 10 ⊧	γ-Carotene [7]	533·5, 496, 463.
⊧′ + 9 ⊧ + ⊧′	β-Carotene [8]	520, 484, 452.
⊧′ + 9 ⊧	α-Carotene [8]	511, 478, 466.
9 ⊧	Oxy-α-Carotene [9]	502, 471, 440.

* ⊧′ *Indicates a conjugated cyclic ethenoid linkage.*

[1] Kuhn and Grundmann, Ber. 1932, 65, [B], 898.
[2] *Idem.*, *ibid.* 1932, 65, [B], 1880.
[3] Zechmeister and Cholnoky, Annalen, 1935, 516, 30.
[4] Kuhn and Brockmann, Ber. 1933 66, [B], 1319.
[5] *Idem.*, *ibid.* 1932, 65, [B], 898.
[6] Karrer and Solmssen, Helv. Chim. Acta, 1935, 18, 25.
[7] Kuhn and Brockmann, Ber. 1933, 66, 407.
[8] Kuhn and Lederer, Z. physiol. Chem. 1931, 200, 246.
[9] Karrer, Euler, and Solmssen, Helv. Chim. Acta, 1934, 17, 1169.

MOLECULAR STRUCTURE OF THE CAROTENOIDS.

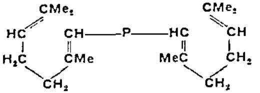
A. Plant Carotenoids.—*Hydrocarbons.*—Carotene (*q.v.*) The tomato pigment *lycopene* has the acyclic structure (I) p. 400 (Karrer and Widmer, Helv. Chim. Acta, 1928, 11, 751 ; Karrer and Bachmann, *ibid.* 1929, 12, 285 ; Karrer, Helfenstein and Wehrli *ibid.* 1930, 13, 87 ; Karrer, Helfenstein. Wehrli and Wettstein, *ibid.* 1930, 13, 1084 ; Karrer, Helfenstein, Pieper and Wettstein, *ibid.* 1931, 14, 435).

Alcohols or Xanthophylls.—The leaf xanthophyll described by Willstätter and Mieg (*l.c.*) is a mixture, the principal component being identical with the pigment from egg yolk (Kuhn, Winterstein, and Lederer, Z. physiol. Chem. 1931, 197, 141). The name *lutein* is retained for this latter lipochrome, the term " xanthophyll " being used to designate the carotenoid alcohols as a class. Three monohydroxy xanthophylls, $C_{40}H_{56}O$, have been characterised. *Kryptoxanthin* (II) occurs in berries of the *Physalis* species (Kuhn and Grundmann, Ber. 1933, 66, [B], 1746) in yellow maize (*ibid.* 1934, 67, [B], 593) and in the orange, *Citrus Aurantium* (Zechmeister and Tuzson, *ibid.* 1936, 69, [B], 1879), *rubixanthin* (III) is obtained from the hips of the dog-rose (*Rosa canina*) (Kuhn and Grundmann, *ibid.* 1934, 67, [B], 339, 1133), and *lycoxanthin* (VII) from bitter-sweet (*Solanum Dulcamara*) (Zechmeister and Cholnoky, *ibid.* 1936, 69, [B], 422).

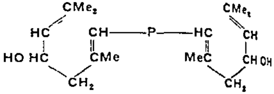
With the exception of carotene, the most abundant lipochrome pigments found in nature are the dihydroxyxanthophylls; *lutein* (V) (Kuhn, Winterstein and Lederer, Z. physiol. Chem. 1931, 197, 141) is found in leaf foliage and in egg-yolk, whilst the isomeric *zeaxanthin* (*see* p. 273) also occurs in many species of leaves and fruits. It is most readily isolated from maize (*Zea Mays*) (Karrer, Wehrli, and Helfenstein, Helv. Chim. Acta, 1930, 13, 268,; Kuhn, Winterstein, and Kaufmann, Ber. 1930, 63, [B], 1489). The aliphatic analogue *lycophyll* (VI) has recently been isolated by Zechmeister and Cholnoky (*ibid.* 1936, 69, 422) from bittersweet (*Solanum Dulcamara*).

Owing to their relative inaccessibility xanthophylls containing 3 oxygen atoms have not been investigated in any great detail. In the case of flavoxanthin, $C_{40}H_{56}O_3$, which is obtained from the buttercup (*Ranunculus acer*), the 3 oxygen atoms have been characterised as hydroxyl groups (Kuhn and Brockmann, Z. physiol. Chem. 1932, 213, 192). *Antheraxanthin*, from the pollen sacs of the tiger lily (*Lilium tigrinum*) (Karrer and Oswald, Helv. Chim. Acta, 1935, 18, 1303) and *petaloxanthin*, from the blossom of *Cucurbita Pepo* (Zechmeister, Béres, and Ujhelyi, Ber. 1936, 69, [B], 573), both of which are formulated as $C_{40}H_{56}O_3$, have been described.

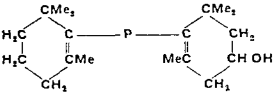
Two tetra-oxygenated xanthophylls have been recognised in *violaxanthin*, $C_{40}H_{56}O_4$, most readily obtained from the pansy (*Viola tricolor*) (Kuhn and Winterstein, *ibid.* 1931, 64, 326 ; Karrer and Solmssen, Helv. Chim. Acta, 1936, 19, 1024), and *taraxanthin*, $C_{40}H_{56}O_4$, from the dandelion (*Taraxacum officinale*) (Kuhn and Lederer, Z. physiol. Chem. 1931, 200, 108).



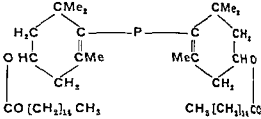
I Lycopene.



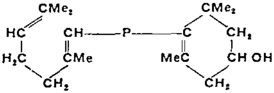
VI. Lycophyll



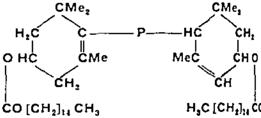
II Kryptoxanthin



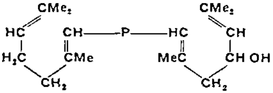
VII Physalien



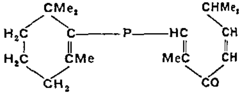
III Rubixanthin



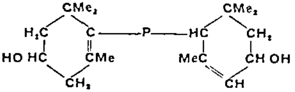
VIII Helenien



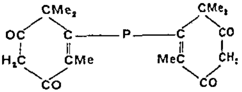
IV. Lycoxanthin



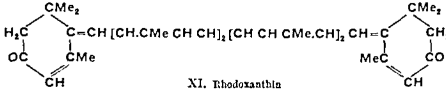
IX. Myxoxanthin



V. Lutein



X Euglenarhodone.



XI. Rhodoxanthin

$$\begin{array}{l} \mathrm{CH\ CH.CMe\ CH\ CH{\cdot}CH\ CMe\ CO_2H} \\ \| \\ \mathrm{CH\ CH\ CMe\ CH.CH\ CH\ CMe\ CO_2H} \end{array}$$

XII. Crocetin.

P = the polyene chain ($C_1 - C_{18}$) in β carotene (p 396)

Of the more highly oxygenated members of this series mention may be made of the algal carotenoids *fucoxanthin*, $C_{40}H_{56}O_6$, the characteristic pigment of brown seaweed (*see* ALGÆ) (Willstätter and Page, Annalen, 1914, **404**, 237 ; Heilbron and Phipers, Biochem. J. 1935, **29**, 1369), and *myxoxanthophyll*, $C_{40}H_{56}O_7$ (Heilbron and Lythgoe, J.C.S. 1936, 1376) from *Oscillatoria rubrescens*, a blue-green alga.

Esters.—The xanthophylls exist in the plant cell both free and as esters of the fatty acids. Thus *physalien* (VII), the dipalmitate of zeaxanthin (p. 273), was isolated by Kuhn and Wiegand, (Helv. Chim. Acta, 1929, **12**, 499) from the berries of the *Physalis* species, and *helenien* (VIII), the dipalmitate of lutein, from *Helenium autumnale* (Kuhn and Winterstein, Naturwiss. 1930, **18**, 754).

Ketones.—The pigment of the red yew berry (*Taxus baccata*) has been shown to be a diketone, *rhodoxanthin* (XI) (Kuhn and Brockmann, Ber. 1933, **66**, 828). Zechmeister and Cholnoky (Annalen, 1934, **509**, 269 ; 1935, **516**, 30) have shown that two closely related hydroxy-ketones, *capsanthin* and *capsorubin* (*see* p. 273), occur together with zeaxanthin in Spanish red pepper or paprika (*Capsicum annuum*). Two ketonic carotenoids have recently been isolated from lower forms of plant life—*myxoxanthin* (IX) from the alga, *Oscillatoria rubrescens* (Heilbron and Lythgoe, *l.c.*), and *euglenarhodone* (X) from *Euglena sanguinea* (Tischer, Z. physiol. Chem. 1936, **239**, 257).

Plant Lipochromes of Molecular Complexity less than C_{40}.—The carotenoids described above all contain 40 carbon atoms in the molecule. Several naturally occurring carotenoids, however, have been isolated which are of considerably lower molecular complexity. With the exception of *citraurin*, recently isolated from the orange (*Citrus Aurantium*) (Zechmeister and Tuzson, Ber. 1936, **69**, 1878) and which is presumed to be an aldehyde, these related pigments are carboxylic acids. *Bixin*, $C_{25}H_{30}O_4$ (*see* Vol. I, p. 378), is the colouring matter of annatto seeds (*Bixa Orellana*), and *crocetin*, $C_{20}H_{24}O_4$ (XII) is the pigment derived from saffran (*Crocus sativus*) (Karrer, Benz, Morf, Raudnitz, Stoll and Takahashi, Helv. Chim. Acta, 1932, **15**, 1218, 1399 ; Kuhn and Winterstein, Ber. 1932, **65**, 646 ; Karrer and Salomon, Helv. Chim. Acta, 1927, **10**, 397). *Azafrin*, $C_{27}H_{38}O_4$ (*see* p. 396), is isolated from the azafranillo root (*Escobedia scabrifolia*) (Kuhn and Deutsch, Ber. 1933, **66**, 883 ; Kuhn and Brockmann, Annalen, 1935, **516**, 95). Kuhn and Winterstein (Ber. 1932, **65**, 646 ; Naturwiss. 1933, **21**, 527) have suggested that the true carotenoids (C_{40}) and those of smaller complexity are phytochemically related in that the latter are formed by the oxidation of the former. This relationship is pictorially illustrated at top of next column.

It is of great interest to note that the degradation both of lycopene to *nor*bixin (Kuhn and Grundmann, Ber. 1932, **65**, 898, 1880) and of β-carotene to a derivative of azafrin (Kuhn and Brockmann, Annalen, 1935, **516**, 95) have been experimentally realised.

←———— C_{40} ————→

Carotene

← C_8 → ← C_{21} → ← C_8 →

Methyl heptenone	Bixin	Methyl heptenone

← C_{10} → ← C_{20} → ← C_{10} →

Picrocrocin	Crocetin	Picrocrocin

← C_{27} → ← C_{13} →

Azafrin	Ionone

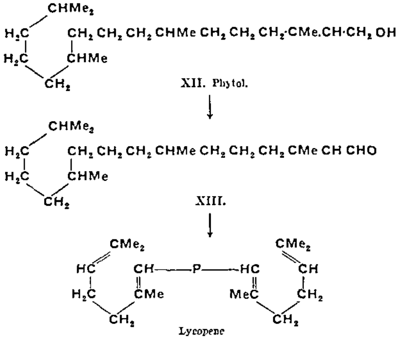
Animal Carotenoids.—The extensive researches of Zechmeister and his collaborators have shown that the more abundant carotenoids of mammalian tissue are the carotenes, lutein, and zeaxanthin, which are the typical carotenoids of green foliage. Only in the lower forms of animal life are distinct carotenoids found which so far have not been detected in plant tissue ; thus astacin (see Vol. I, p. 532) is the characteristic pigment of the crustaceæ (Kuhn and Lederer, Ber. 1933, **66**, 488 ; Karrer and Benz, Helv. Chim. Acta, 1934, **17**, 412 ; Karrer and Loewe. *ibid.* 745 ; Karrer, Loewe, and Hübner, *ibid.* 1935, **18**, 96).

The sea anemone (*Actinia equina*) contains a xanthophyll-ester, *actinioerythrin*, hydrolysis of which gives the pigment *violerythrin* (Fabre and Lederer, Bull. Soc. Chim. biol. 1934, **16**, 105 ; Heilbron, Jackson, and Jones, Biochem. J. 1935, **29**, 1384). Many other animal carotenoids such as *cynthiaxanthin*, *glycymerin*, *pentaxanthin*, *pectenoxanthin*, and *echinenone* have been described in the last few years, but the nature and even the entity of many of these is doubtful (*see* Lederer, "Les Caroténoids des Animaux," Paris, 1935, for a more complete review).

Carotenoids of Bacteria.—Rhodovibriobacteria (purple bacteria) contain a series of carotenoid pigments. Of these, only *rhodoviolascin*, $C_{42}H_{60}O_2$, has been clearly characterised. It is of great interest in being the only non-hydrolysable carotenoid pigment so far isolated which contains more than 40 carbon atoms. The two extra carbon atoms are present as methoxyl groups (Karrer and Solmssen, Helv. Chim. Acta, 1935, 18, 1306 ; 1936, 19, 3).

BIOSYNTHESIS OF THE CAROTENOIDS.—Two general principles of carotenoid chemistry are to be noted from a study of the molecular formulæ (I)–(X). First, they all contain a long chain of conjugated ethylenic linkages, *in most cases terminated* by an ionone ring. Secondly, the polyene chain carries methyl group attachments, at regular intervals, in such a manner that the whole molecule can be dissected into isoprene units. The carotenoids are thus polyterpenoid in nature. From the complete symmetry of the lycopene molecule, it is clear that the fusion of eight isoprene units cannot be effected in the normal "head-tail" manner but rather by such a condensation of four units and the self-condensation of two of the

C_{20} fragments so formed. With this in mind, Karrer, Helfenstein, Wehrli, and Wettstein (Helv. Chim. Acta, 1930, 13, 1084) suggested that the phytosynthesis of carotenoids may be effected by the condensation of 2 mols. of the aldehyde (XIII) related to phytol (XII) (Fischer and Löwenberg, Annalen, 1929, 475, 183) followed by dehydrogenation to give lycopene.



XII. Phytol.

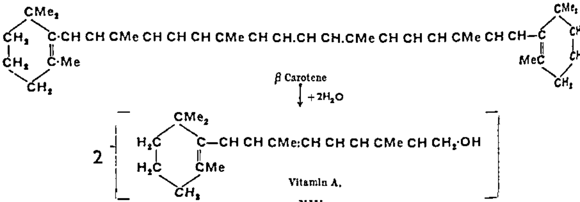
XIII.

Lycopene

P = the polyene chain ($C_1 - C_{13}$) in β carotene (p 396)

PHYSIOLOGICAL IMPORTANCE OF THE CAROTENOIDS —The extensive investigations of Steenbock and his collaborators (Steenbock, Science, 1919, 50, 352 ; Steenbock and Boutwell, J Biol. Chem 1920, 41, 81, 131 , Steenbock and Sell, *ibid.* 1922, 51, 63) indicated a connection between the vitamin A activity of plant materials and their carotene content, but it was not until 1929 that full substantiation of Steenbock's view was forthcoming from the experiments of von Euler, who proved that carotene can replace vitamin A in the diet of animals (von Euler and von Euler, Svensk Kem. Tidskr 1928, 40, 242 ; von Euler, von Euler, and Hellstrom, Biochem Z 1928, 203, 370; von Euler, von Euler, and Karrer, Helv Chim Acta, 1929, 12, 278) Later, Moore (Biochem J 1929, 23, 803, 1267, 1930, 24, 692) showed that whereas the liver oil of rats suffering from vitamin A deficiency gave no characteristic vitamin reactions, when the diet of the animals was supplemented by carotene, vitamin A accumulated in the liver. These experiments, which have been fully confirmed by other workers, show that carotene is converted into vitamin A in the animal organism.

The most prolific and accessible sources of vitamin A are the liver oils of the cod and halibut. The vitamin prepared from such sources is a highly viscous, nearly colourless oil characterised by its intense absorption in the ultraviolet with maximum at $328 m\mu$, and by the blue coloration which it gives with antimony trichloride. Vitamin A (XIV) (Karrer, Morf, and Schopp, Helv. Chim. Acta, 1931, 14, 1036) is a primary alcohol containing a system of five conjugated ethylenic linkages and its relationship to β carotene is represented by the equation :



β Carotene

$+2H_2O$

Vitamin A.

XIV.

In support of this relationship Kuhn (Z. physiol. Chem. 1933, **221**, 129) has shown that β-carotene is approximately twice as physiologically potent as either α- or γ-carotene and furthermore it has been shown (Kuhn and Brockmann, Annalen, 1935, **516**, 95) that all the degradation products of β-carotene in which one half of the molecule remains intact and unsubstituted, possess vitamin A activity.

I. M. H., R. F. P. and F. S. S.

CAROUBIN and CAROUBINOSE. The caroubin and caroubinose described by Effront (Compt. rend. 1897, **125**, 38, 116) are mannan and *d*-mannose respectively (van Ekerstein, Compt. rend. 1897, **125**, 719).

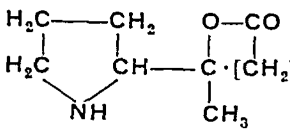
CARPAINE, $C_{14}H_{25}O_2N$ (I), was first isolated from *Carica Papaya* (N.O. Caricaceæ) by Greshoff (Meded. uit's Plantentuin, 1890, **7**, 5) and afterwards by Wester (Chem. Zentr. 1914, I, 1353) from *Vasconcellea hastata* (Caricaceæ). For history, botanical details, and early chemical literature, *cf.* van Rijn (Arch. Pharm. 1893, **231**, 184 ; *ibid.* 1897, **235**, 332).

van Rijn (*l.c.* 1893) gives a detailed description for the extraction of dried papaya leaves. The yields of (I) vary considerably—old leaves give less alkaloid (0·07%), young leaves considerably more (Greshoff, *l.c.* 0·25%) ; Barger, Girardet and Robinson (Helv. Chim. Acta, 1933, **16**, 90) found less (I): young leaves of older trees 0·036%, seedlings specially grown 0·022%).

(I) crystallises in monoclinic prisms, m.p. 121°, b.p. 215°–235°, $[\alpha]_D$ +21°55′ in alcoholic solution; it is easily soluble in most organic solvents, but not in light petroleum or in H_2O. B·HCl m.p. 225°, and $B{\cdot}H_2SO_4,3H_2O$ soluble in H_2O ; B·HBr, B·HI, and $B{\cdot}HNO_3$ sparingly soluble in H_2O ; $B{\cdot}HAuCl_4,5H_2O$, yellow needles, m.p. 205° (dry, from alcohol). Nitrosocarpaine crystallises from alcohol in small, colourless prisms, m.p. 144°–145° ; N-methylcarpaine, small prisms, m.p. 71° (from dilute alcohol).

Barger (J.C.S. 1910, **97**, 466) prepared *carpamic acid* (long needles, m.p. 224°, from alcohol-acetone) by acid and alkaline hydrolysis of (I) and suggested the presence of a lactone ring. Barger, Girardet and Robinson (*l.c.*) definitely identified suberic and azelaic acids respectively as oxidation products. They also obtained evidence for the presence of a pyrrolidine ring.

Barger, Robinson and Work (J.C.S. 1937, 711) conclude that carpaine has the following structure:



Carpamic acid is a tertiary alcohol; hydriodic acid and phosphorus reduce it to a hydrocarbon and ammonia. By exhaustive methylation and reduction an acid, $C_{14}H_{28}O_3$, is obtained. This acid and the hydrocarbon, like carpaine itself, contain one C-methyl group. By the action of phosphorus pentachloride, followed by alcoholic potassium hydroxide, anhydro carpamic acid is obtained, which on ozonisation yields an acid, probably

$$CH_3{\cdot}CO{\cdot}[CH_2]_7{\cdot}COOH,$$

and on oxidation with permanganate, azelaic acid. The large lactone ring has so far prevented the conversion of tasteless carpamic acid to the very bitter carpaine. For pharmacological action of carpaine, *cf.* van Rijn (*l.c.* 1893, **231**, 184), Alcock and Meyer (Arch. f. Physiol. 1903, 225), Kakowski (Arch. intern. pharmac. thérapie, 1905, **15**, 84), and Tu (Ber. ges. Physiol. u. Exper. Pharmakol. 1926, **37**, 910).

Schl.

CARPILINE. A name given by Léger-Roques to *filosine*, one of the Jaborandi alkaloids.

CARPOTROCHE OIL. Oil of *Carpotroche brasiliensis*, forms 63–69% of the seed, $[\alpha]_D^{20}$ +58·9° in chloroform, n^{25} 1·4792, acid value 0·4, iodine value 112·8, saponification value 201. (Jamieson, 1932, A, 515).

CARRAGHEEN (alternatively Carrageen, Caragheen). Carragheen, known as Irish Pearl Moss, is the common name for the red alga *Chondrus crispus* Stackhouse (Fam. Gigartinaceæ), which is exposed at low spring tides. Carragheen is marketed in yellow translucent strips of 5–30 cm. in length ; it is almost completely soluble in hot water, the solution setting to a jelly on cooling. The jelly is used as a demulcent, as a size substitute, as a protective colloid, and to emulsify cod-liver oil. De Jong and Gwan (Kolloid Chem. Beih. 1929, **29**, 435) showed that solutions of carragheen possess an unusually high viscosity. Carragheen contains 90% dry matter known as *carragheenin* which is probably allied to pectin. Carragheenin, which is coagulated by azine and thiazine dyes (Justin-Mueller, Bull. Soc. chim. 1924, **35**, 390) may be assayed by precipitation with benzidine hydrochloride solution (Haas and Russell-Wells. Analyst, 1927, **52**, 205). It is a mixture of two substances, one soluble in hot water to give a viscous solution which does not set to a gel on concentration and cooling, and the other slightly soluble in hot water and setting to a gel on cooling (Haas and Russell-Wells, Biochem. J. 1921, **15**, 469 ; 1922, **16**, 578 ; 1929, **23**, 425).

I. M. H., R. F. P. and F. S. S.

CARROT, the tapering tap-root of *Daucus carota*, Linn. Red varieties are commonly used for domestic purposes and the white (or Belgian) type, although not very extensively used, are valued in some districts for feeding horses and dairy cattle. The following are typical analyses:

	H_2O %	Protein %	Fat %	N-free extract %	Fibre %	Ash %
Kellner . .	87·0	1·2	0·2	9·3	1·3	1·0
Lindsey *et al.*[1] . .	89·0	1·0	0·1	7·9	1·0	1·0

[1] Massachusetts Agric. Exp. Sta. Bull. 1919.

According to Platenius (Plant Physiol. 1934, **9**, 671 ; Cornell Univ. Agric. Exp. Sta. Mem. 1934, No. 161, 3–18) variations in composition of carrots during growth are small in comparison with those of many other root crops. The fibre and total carbohydrate contents increase somewhat, and the protein content tends to decline

with advancing age. Of the sugars only sucrose and glucose are present, the former increasing at the expense of the latter as growth proceeds. Starch is present at all stages of growth. Falk (Ind. Eng. Chem. 1919, **11**, 1133) gives the following data for the carbohydrates of fresh carrots in terms of percentage of total: Reducing sugars before hydrolysis 57·1, dextrin and soluble starch 2·7, insoluble starch 5·1, total reducing sugars after hydrolysis 92·2%. Siebelin (Chem.-Ztg. 1906, **30**, 401) reports 8·43% of pentosans and 2·59% of methyl pentosans in the dry matter of carrots. The flavour of carrots is closely associated with the sucrose content (Platenius, *l.c.*). The stile or central core of the carrot contains a larger proportion of protopectin than does the cortex although the true pectin content of both parts is very similar (Buston and Kirkpatrick, Ann. Bot. 1931, **45**, 519).

The colouring matter of red varieties consists largely of α- and β carotene, which is also present in smaller amounts in the leaves (Mackinney and Milner, J. Amer. Chem. Soc. 1933, **55**, 4728). As a vitamin source carrots rank highly in respect of A, are a fairly good source of B, but contain rather small proportions of C. Storage of carrots does not involve serious loss of vitamin potency, but vacuum drying causes approximately 80% loss of vitamin A (Fraps and Treichler, J. Agric. Res 1933, **47**, 539).

According to Snyder (U.S. Dept. Agric. Off. Exp. Sta. Bull. 1897, No. 43, 7 pp), there is considerable loss of nutrient value on boiling carrots. This loss may amount to 20–30% of the total solids, 20–40% of the total nitrogen, 15–26% of the sugars, and 30–45% of the ash constituents. Huskins (Massachusetts Agric. Exp. Sta. Spec. Bull 1919. No. 95) records the ash analysis of carrots as: total ash 0·92, K_2O 0·51, Na_2O 0·06, CaO 0·07, MgO 0·02, and P_2O_5 0·09% of the fresh vegetable. The proportions of trace elements reported by various investigators include Fe 2·2–6·4, Al 2·2–3·0, Mn 1·9–9·1, Cu 0·7–2·2, Zn 2·9–4·3, As 0·05 mg. per kg. of fresh roots.

Carrot seeds yield an essential oil on steam distillation which is used in perfumes and liqueurs, and contains pinene, *l* limonene, butyric, *iso*-butyric, and acetic esters, daucol ($C_{15}H_{26}O_2$), caratol ($C_{15}H_{26}O$), asarone, and bisabolene (W. S. Guenther, Amer. Perfumer, 1936, **31**, No. 5, 7). Richter (Arch. Pharm. 1909, **247**, 391) examining the seed oil of wild carrot reports the following characteristics d^{15} 0·9439, $[\alpha]^{15}$ −13·38°, saponification value 20·26, ester value 18·22, acid value 204. Asahina and Tsukamoto (J. Pharm. Soc. Japan, 1925, **525**, 961), however, give the values (possibly of a different variety) as d^{22} 0·9088, $[\alpha]_D^{22}$ −5·98°, saponification value 74·08, and acid value 0.

A vegetable oil was also obtained from the seed by Reeb (J. Pharm. Alsace-Lorraine, 1923, **50**, 13). Its bitter flavour is ascribed to the presence of a yellow glucoside daucusin.

A. G. Po.

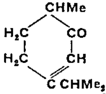
CARTHAMIN. The red colouring matter of Safflower, yields on hydrolysis glucose and *carthamidin*, 5:7:8:4′-tetrahydroxyflavanone.

CARVASEPT is chlorocarvacrol, 2 methyl 4-chloro-5 *iso*propyl phenol,

$$HO{\cdot}C_6H_2ClMePr^{\beta}$$

CARVENENE, $\Delta^{1:3}$-dihydrocymene (Wallach's α terpinene) has m.p. 162°–162·5°, b.p. 61°–63°/10 mm , 179·5°–180·5°/735 mm., d_{20}^{20} 0·844, n_D 1·49100 (Harries and Majima, Ber. 1908, **41**, 2516, Semmler, *ibid.* 4474; *ibid.* 1909, **42**, 4171).

CARVENONE.

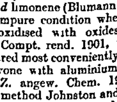


The ketone *carvenone*, $C_{10}H_{16}O$, b p. 232°–233°, d_4^{20} 0·9266, n_D^{20} 1·48245, does not occur in nature. It is formed by the action of sulphuric acid and other dehydrating agents on camphor (Delalande, L'Institut, 1839, 399; Chataud, Compt rend. 1857, **44**, 66; Schwanert, Annalen, 1862, **123**, 298; Armstrong and Kipping, J C S. 1893, **63**, 75; Marsh and Gardner, *ibid.* 1897, **71**, 285; Marsh and Hartridge, *ibid.* 1898, **73**, 852; Bredt, Rochussen, and Monheim, Annalen, 1901, **314**, 374).

Its structure is proved by its conversion into carvacrol by oxidation with ferric chloride (Wallach, Annalen, 1895, **286**, 134) and by its oxidation with potassium permanganate to α-methyl α-*iso*propyl-α′-hydroxyadipic acid, a methyl γ *iso*butyrylbutyric acid, and α methyl glutaric acid (Tiemann and Semmler, Ber. 1898, **31**, 2889). Wallach (Annalen, 1924, **437**, 145) has shown the primary product of oxidation to be diosphenol. Its oxidation with hydrogen peroxide in alkaline solution has been studied by Treibs (Ber. 1932, **65**, [B], 163; 1933, **66**, [B], 1484). Carvenone is reduced by aluminium *iso*propoxide to the secondary alcohol *carvenol*, b.p 99°–102°, 14 mm , n_D^{17} 1·4799, 3 5-*dinitrobenzoate*, m p. 75°–76° (Johnston and Read, J.C.S 1934, 237) This alcohol has been prepared also by Wallach (Annalen, 1917, **434**, 203) from the dicyclic alcohol sabinol.

J. L. S

CARVEOL.



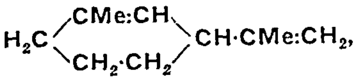
The alcohol *carveol*, $C_{10}H_{16}O$, occurs in small quantity in oil of caraway (from the fruits of *Carum carvi*) (Blumann and Zeitschel, Ber. 1914, **47**, 2628). It is formed during the autoxidation of *d* limonene (Blumann and Zeitschel) and in an impure condition when this hydrocarbon is oxidised with oxides of nitrogen (Genvresse, Compt. rend. 1901, **132**, 414). It can be prepared most conveniently by the reduction of carvone with aluminium *iso*propoxide (Ponndorf, Z. angew. Chem. 1926, **39**, 138) and by this method Johnston and Read (J.C.S. 1934, 233) have prepared *d*- and *l*-*cis* carveols, m p. 24°–25°, b p. 101·2°–101·4°/10 mm , d_4^{15}

0·9521, n_D^{25} 1·4959, $[\alpha]_D^{25}$ ±23·9°; 3:5-*dinitrobenzoate*, m.p. 92·5°; *d*- and *l*-*trans*-carveols, b.p. 102·2°–102·4°/10 mm., d_4^{25} 0·9484, n_D^{25} 1·4942, $[\alpha]_D^{25}$ ±213°; 3:5-*dinitrobenzoate*, m.p. 111·5°. The dl-cis- and trans-3:5-*dinitrobenzoates* melt respectively at 91·5° and 119°. A dl-*phenylurethane*, m.p. 94°–95°, and a *hydrogen phthalate*, m.p. 136°–137°, have been described, but it is not known to which series they belong.

On oxidation with chromic acid the alcohols yield carvone, whilst on catalytic hydrogenation a mixture of carvomenthols (*q.v.*) is obtained.

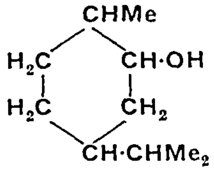
J. L. S.

CARVESTRENE, $\Delta^{1:8(9)}$-*m*-menthadiene,

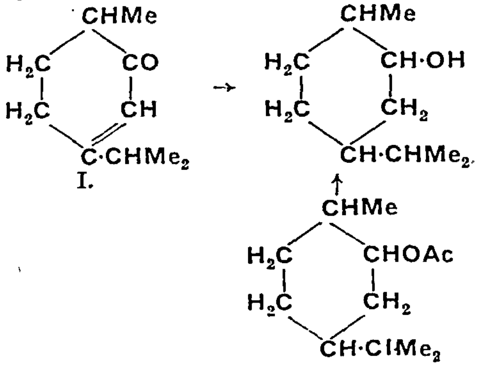


is *dl*-sylvestrine, the synthetic isomer of *d*-sylvestrine. It is a liquid, b.p. 178°–179°/750 mm., has a pungent odour of lemons, and its solution in acetic anhydride is coloured a deep methylene blue on the addition of a drop of sulphuric acid (Perkin and Tattersall, J.C.S. 1907, 91, 480).

CARVOMENTHOL.



The secondary alcohol *carvomenthol*, $C_{10}H_{20}O$, known also as *tetrahydrocarveol*, does not occur in nature. It was prepared first by Wallach (Annalen, 1893, 277, 130) by the reduction of *carvenone* (I), and by Baeyer (Ber. 1893, 26, 822) by the reduction of the *acetyl* derivative of *dihydrocarveol hydroiodide* (II), followed by hydrolysis of the acetate.



I. II.

The alcohol can be prepared also by the reduction of the phenol carvacrol (Brunel, Compt. rend. 1903, **137**, 1269; 1905, **141**, 1246), the ketones carvone, carvotanacetone, and carvomenthone, and the alcohols carveol and dihydrocarveol. Carvomenthol is a viscid oil, and since it contains three centres of asymmetry it can exist in eight optically active and four externally compensated modifications. An attempt to separate these was made by Paolini (Atti R. Accad. Lincei, 1921 [v], **28**, II, 82, 134; Gazzetta, 1925, **55**, 818), but the pure alcohols were first obtained by Johnston and Read (J.C.S. 1934, 230; 1935, 1138), who prepared the alcohols (*a*) from *l*-carvomenthone and *l*-*iso*-carvomenthone *via* the oximes and carvomenthylamines, (*b*) by the hydrogenation of *d*-dihydrocarveol and *l*-*neo*dihydrocarvone, and (*c*) by the hydrogenation of *d*-*cis* and *trans*carveols. The constants of these alcohols and those of their derivatives are given in the tables below:

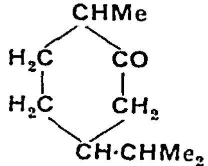
	d-Carvomenthol.	*l*-*neo*Carvomenthol.	*l*-*iso*Carvomenthol.	*l*-*neoiso*Carvomenthol.
b.p. . . .	101·8°–102°/14 mm.	102°/18 mm.	106°/17 mm.	—
d_4^{20} . . .	0·9056/13°	0·9012	0·9109	0·9102
n_D^{20} . . .	1·4650/12°	1·4632	1·4662	1·4676
$[\alpha]_D$ . . .	+27·69°	−41·70°	−17·72°	−34·7°
3:5-dinitrobenzoate, m.p. .	107°	129°	111°	71°–72°
p-nitrobenzoate, m.p. .	—	95°	64·5°	54°–55°

	dl-*neo*-Carvomenthol.	*dl*-*isoneo*-Carvomenthol.
b.p. . .	105°–109°/20 mm.	110°/20 mm.
d_4^{20} . . .	—	0·904
n_D . . .	1·4637/26°	1·4469/18°
$[\alpha]_D$ . .	±0°	±0°
3:5-dinitrobenzoate, m.p. . .	106°	94·5°
p-nitrobenzoate, m.p.	91°–92°	—

On oxidation with Beckmann's reagent *d*-carvomenthol and *l*-*neo*carvomenthol give *l*-carvomenthone, *l*-*iso*carvomenthol gives *l*-*iso*-carvomenthone.

J. L. S.

CARVOMENTHONE.



The ketone *carvomenthone*, $C_{10}H_{18}O$, known also as *tetrahydrocarvone*, occurs in nature in its lævorotatory form, in the oil from *Blumea Malcolmii* (Simonsen and Rau, J.C.S. 1922, 121, 881). It has b.p. 218·5°–219°/750 mm. d_{20}^{30} 0·9001, n_D^{20} 1·4531, $[\alpha]_D$ −9·33°. It was prepared originally by Wallach (Annalen, 1893, 277, 133)

and Baeyer (Ber. 1893, 26, 822) by the oxidation of the secondary alcohol, *carvomenthol* (*q v.*). It can be prepared also by the hydrogenation of the unsaturated ketones, carvone, dihydrocarvone, carvotanacetone, and carvenone.

Containing as it does two centres of asymmetry, carvomenthone should exist in two optically active and two externally compensated forms. Johnston and Read (J C.S. 1934, 226, 1935, 1142) have described l-*carvomenthone* and l *isocarvomenthone*. The former was obtained by the oxidation of *d*-carvomenthol with Beckmann's reagent and the latter from *l isocarvomenthol*. The constants and derivatives of these ketones are given in the table:

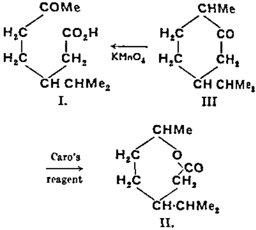
	l Carvomenthone.	*l iso*Carvomenthone.
b p. . . .	96°–96 5°/16 mm	—
d_4^{20} . . .	—	0 9102
n_D . . .	1 4548/17°	1 4558/20°
$[\alpha]_D$ . .	−6°	−56 5°
Oxime, m p. .	99°–100°	liquid
$[\alpha]_D$ (in alcohol) .	−38 7°	−79 5°
Semicarbazone, m p. . .	192°	171°–172°
$[\alpha]_D$ (in chloroform) . .	−13 3°	−117°

The equilibrium mixture, which is formed when either of the ketones is kept with cold sodium ethoxide, contains about 80% of *l*-carvomenthone.

For *dl*-carvomenthone, which contained probably some *dl isocarvomenthone*, Wallach and Baeyer found b p. 210°–221°, d^{20} 0 90, n_D 1 4554, *oxime*, m.p. 105°, *semicarbazone*, m.p. 174°, *nitroso*-derivative, m.p. 119°.

The ketone has been prepared synthetically by Ruzicka and Trebler (Helv. Chim. Acta, 1920, 3, 779) by the action of sodium on methyl α methyl δ *iso*propyladipate, the cyclic keto-ester formed yielding carvomenthone on hydrolysis.

By the oxidation of carvomenthone (III) with potassium permanganate, Baeyer (Ber. 1896, 29, 36; 1899, 32, 3629; 1900, 33, 124) obtained 2-*isopropylheptane-5-onoic acid*, m.p. 40° (I), whilst with Caro's reagent the lactone (II) was obtained.

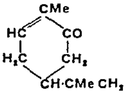


By the reduction of carvomenthoxime Wallach (Annalen, 1893, 277, 134; 1895, 287, 159, 377; 1900, 312, 203; 1902, 323, 332) prepared *carvomenthylamine*. The stereoisomeric bases have been studied in greater detail by Johnston and Read (*l c.*), who have prepared the pure bases listed below:

	d Carvomenthylamine	*l-neo*Carvomenthylamine	*l-iso*Carvomenthylamine
b.p.	89 8°–90°/16 5 mm.	87 8°–88°/15 mm.	90°/15 mm.
d_4^{25}	0 8505	0 8558	0 8587
n_D^{25}	1·4578	1·4596	1 4611
$[\alpha]$	+12 47°	−26 55°	−14·7°
Acetyl, m p. . . .	160°–161°	114°	96°
$[\alpha]_D$ (in chloroform) .	+67 8°	−61 9°	−57·4°

J. L. S

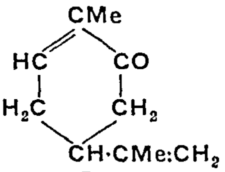
CARVONE.



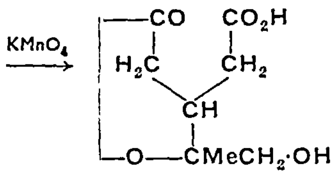
The cyclic ketone *carvone*, $C_{10}H_{14}O$, occurs fairly widely distributed in nature and it is found in *d*-, l-, and *dl*- forms. It is the main ketonic constituent of caraway and dill oils. Carvone is a somewhat viscid, colourless oil with a highly characteristic odour. It is most conveniently separated from essential oils by means of the compound which it forms with hydrogen sulphide, *d*- and *l*- m p. 210°–211°, *dl*- m p. 188°–190° (Deussen, J. pr. Chem. 1914, [ii], 90, 315). The structure of carvone hydrosulphide has been discussed by Hooper, Macbeth, and Price (J.C S. 1934, 1147), by Dulou (Bull. Inst. Pin, 1934, 60, 204), and by Padmanabhan (Current Sci. 1935, 4, 95). The ketone can be regenerated from the hydrosulphide by the action of alkali. The following constants have been recorded: *d*-, b p. 230°/750 mm, $d_4^{18.7}$ 0 9611, $n_D^{18.7}$ 1·49935, $[\alpha]_D$ +62 32°; *l*-, b p. 230°–231°/763 mm., d_{15}^{15} 0 9652, n_D^{20} 1·4988, $[\alpha]_D$ −62 46°;

dl-, b.p. 230°–231°, d_{15}^{15} 0·9645, n_D 1·50030. The d- and l-*oximes* have m.p. 72°–73°, *dl*- m.p. 93°; d- and *l*-*semicarbazones*, m.p. 162°–163°, 141°–142° respectively; *dl*-, m.p. 154°–156°.

Goldschmidt and Zürrer (Ber. 1885, **17**, 1729) made the important observation that carvoxime and nitrosolimonene, prepared by the removal of hydrogen chloride from limonene nitrosochloride, were identical, and in 1894 Wagner (Ber. 1894, **27**, 227) suggested that carvone was represented by (I), which is in accord with its ready conversion into carvacrol and with its oxidation by potassium permanganate to *hydroxyterpenylic acid* (II), which can be reduced by hydrogen iodide to *terpenylic acid* (III) (Tiemann and Semmler, Ber. 1895, **28**, 2148).



I.



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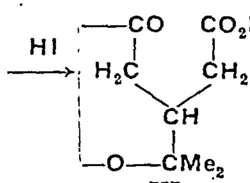
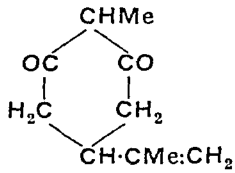


III.

In view of the identity of *dl*-carvoxime with nitrosodipentene, the synthesis of the latter by Perkin (J.C.S. 1904, **85**, 416) implies also a synthesis of the ketone.

Since in addition to the carbonyl group, carvone contains two ethylenic linkages, it is an extremely reactive substance, and yields a number of interesting derivatives. On catalytic hydrogenation it gives, according to the conditions and the nature of the catalyst employed, either *carvomenthone* or *carvomenthol* (*q.v.*) (Haller and Martine, Compt. rend. 1905, **140**, 1308; Ipatiev and Balatschinsky, Ber. 1911, **44**, 3461), whilst with sodium and alcohol it gives *dihydrocarveol* (Wallach, Annalen, 1893, **275**, 111). On reduction with zinc dust in acetic acid *dihydrocarvone* is obtained together with the pinacone *a-dicarvelone* (Wallach, Annalen, 1894, **279**, 377). With aluminium *iso*propoxide as the reducing agent *carveol* is obtained (Ponndorf, Z. angew. Chem. 1926, **39**, 138; Johnston and Read, J.C.S. 1934, 232).

When carvone is shaken with oxygen in the presence of baryta a yellow *diketone* (IV) is obtained (Harries, Ber. 1901, **34**, 2105), the dioxime of which is formed when carvone hydroxylamine-oxime is shaken with mercuric oxide (Harries, J. pr. Chem. 1914, [ii], **90**, 318). This ketone is obtained much more readily by the oxidation of carvone with hydrogen peroxide in alkaline solution, when the primary product is the *oxide* (V) (Treibs, Ber. 1931, **64**, 2178; 1932, **65**, 1314; 1933, **66**, 1484).



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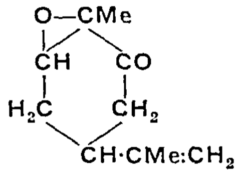
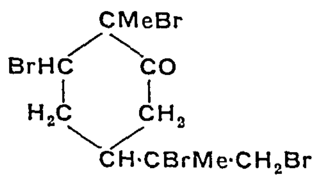


V.

By the bromination of carvone a mixture of crystalline (*d*- and *l*- m.p. 120°–122°, *dl*- m.p. 112°–114°) and liquid *tetrabromides* is obtained; these are probably stereoisomerides having the structure (VI), and yield respectively on further bromination stereoisomeric *pentabromides* (VII), *d*- and *l*- m.p. 86°–87°, *dl*- m.p. 96°; *d*- and *l*- m.p. 142°–143°, *dl*- m.p. 124°–126°) (Wallach, Annalen, 1894, **279**, 290; 1896, **285**, 120). A *tribromide* (VIII) is obtained on bromination in acetic acid in the presence of hydrogen bromide (Wallach, Annalen, 1895, **286**, 119).



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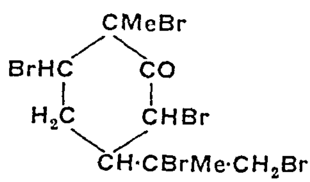
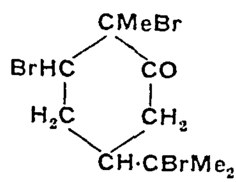
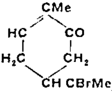


VII.

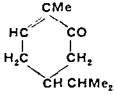


VIII.

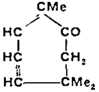
On treatment with hydrogen bromide in acetic acid solution *d*-carvone yields a *hydrobromide* (IX), m p. 32° (Baeyer, Ber. 1894, 27, 811), the *oxime* of which is formed when *d*-carvoxime is treated with hydrogen bromide. Reduction of the bromide with zinc dust in acetic acid solution gives *carvotanacetone* (X), whilst with alcoholic potassium hydroxide it yields *eucarvone* (XI).



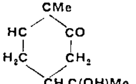
IX.



X.



XI.

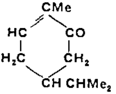


XII.

Whilst carvone is isomerised to carvacrol by the action of dehydrating agents, Rupe and Schlochoff (Ber. 1905, 38, 1719) obtained a *hydroxycarvone*, m p 41°–42° (XII), by treatment of *d* carvone with sulphuric acid (40%).

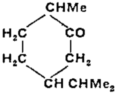
J. L. S

CARVOTANACETONE.

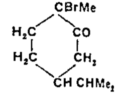


The ketone carvotanacetone, $C_{10}H_{16}O$, occurs in its dextrorotatory form in the oil from the herb *Blumea Malcolmii* (Simonsen and Rau, J C S 1922, 121, 876) and possibly also in thuja oil (from *Thuja occidentalis*) (Wallach, Annalen, 1893, 275, 182) It was obtained originally by Semmler (Ber. 1894, 27, 895) by the molecular rearrangement of the dicyclic ketone *a* thujone, which occurs when this ketone is heated at 280° under pressure. *dl* Carvotanacetone, which is an oil having an odour similar to that of carvone, has b p. 228°–228 5°, d_4^{20} 0 9351, n_D^{20} 1 4805, whilst *d* carvotanacetone has b p 227 5°/705 mm., d_{24}^{30} 0 9305, n_D^{30} 1 4767, $[a]_D$ +59 55°. The ketone, which reacts readily with sodium sulphite in neutral solution, can be identified most readily by the preparation of the *semicarbazone*, *dl*- m p. 177–178°, *d* and *l*- m p 173°–174° (Baeyer, Ber. 1894, 27, 1923). Other characteristic derivatives are the *oxime*, *dl*- m p. 92°–93° ; *d*- and *l* m p 77 ; the *hydroxylamino oxime*, *dl*- m.p 162 , *d*- m p. 95°–96° ; the *hydrosulphide*, *dl*- m.p. 205°, *d*- m p. 221°–225°.

Carvotanacetone can be conveniently prepared by the bromination of carvomenthone (I), the resulting bromide (II) yielding on treatment



I.



II.

with sodium acetate in alcoholic solution an excellent yield of the unsaturated ketone (Kotz and Steinhorst, Annalen, 1911, 379, 13; Wallach, *ibid.* 1918, 414, 353). It is formed also by the reduction of carvone hydrobromide (Harries and Stirm, Ber. 1901, 34, 1924), by the action of potassium hydroxide in the presence of ferric hydroxide on cyanocarvomenthone (Lapworth, J C S. 1900, 89, 1830) and also as the oxime by the catalytic hydrogenation of carvoxime (Wallach, Annalen, 1914, 403, 74). On catalytic hydrogenation the ketone yields carvomenthone (Vavon, Compt. rend 1911, 153, 70), whilst on reduction with sodium and alcohol carvomenthol is obtained (Semmler, Ber. 1894, 27, 895) Oxidation of carvotanacetone with potassium permanganate in alkaline solution results in the formation of pyruvic and *β* isopropylsuccinic acids (Semmler, Ber. 1900, 33, 2451 ; Simonsen and Rau, *l c.*) On oxidation with hydrogen peroxide in alkaline solution it yields an *oxide*, b p 118°–120°/20 mm , d^{20} 1 0129, n_D 1 4735 (Treibs, Ber. 1933, 66, 1483)

J. L. S

CARYOPHYLLENES, THE.

The *caryophyllenes* form the main sesquiterpene hydrocarbons, $C_{15}H_{24}$, present in oil of cloves They occur also in other essential oils. An extensive series of investigations by Deussen (Annalen, 1907, 356, 1 ; 1908, 359, 245 ; 1909, 369, 51 ; 1912, 388, 136 ; J. pr. Chem. 1911, [ii] 83, 483 ; 1914, 90, 324 ; 1926, 114, 63 ; 1927, 117, 273 ; 1928, 120, 133 ; 1929, 122, 201) has shown the probable presence of three distinct hydrocarbons, which have been designated *a*, *β*- and *γ*-caryophyllenes. *a* Caryophyllene is most probably identical with the hydrocarbon *humulene*, present in oil of hops (Chapman, J C S. 1928, 785) and in that from poplar buds (Fichter and Katz, Ber. 1899, 32, 3183) The name humulene is therefore to be preferred for this hydrocarbon, since unlike *β*- and *γ* caryophyllenes it does not yield a crystalline hydrochloride or on hydration a crystalline alcohol.

Humulene, b p. 263°–266°, 132°–134°/16 mm , d_{15}^{15} 0 9001, n_D^{15} 1 5021, is concentrated by repeated fractionation to the extent of about 12–15% in the higher boiling fractions of clove oil and it has been characterised by the preparation of a *nitrosochloride*, m p. 177°, which is apparently optically inactive, a *nitrosobromide*, m p. 144–145°, a *nitrosate*, m.p 161°, and a

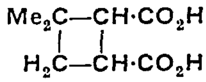
nitrosite, m.p. 116°. The nitrosochloride on treatment with sodium ethoxide or pyridine loses hydrogen chloride with the formation of *nitrosohumulene*, $C_{15}H_{22}ON$, m.p. 126°–127°, which is reduced by sodium and alcohol to *aminodihydrohumulene*, b.p. 141°–143°/11 mm., *acetyl* derivative, m.p. 142° (Evans, Ramage and Simonsen, J.C.S. 1934, 1806). No evidence of the structure of humulene is as yet available, although its physical constants suggest that it is dicyclic. On oxidation with chromic acid it yields *as*-dimethylsuccinic acid (Chapman, J.C.S. 1903, 83, 513).

β-Caryophyllene cannot be separated from *γ*-caryophyllene or from humulene by distillation. It has been characterised by the preparation of a blue *nitrosite*, m.p. 115°, and a *nitrosochloride*, m.p. 159°.

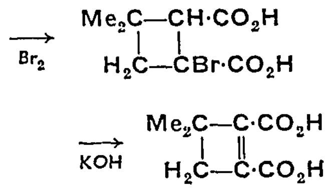
γ-Caryophyllene, b.p. 125°–125·5°/14·5 mm., d^{19} 0·89951, n_D^{19} 1·49665, $[\alpha]_D$ −26·17°, can be separated from the mother liquors remaining after the preparation of *β*-caryophyllene nitrosite and also by heating this nitrosite with alcohol, but there is some doubt as to its homogeneity (Ruzicka and Wind, Helv. Chim. Acta, 1931, 14, 410). It has been characterised by the preparation of two *nitrosochlorides*, m.p. 122° and 146°, each of which gives the same *nitrolbenzylamine*, m.p. 172°–173°, which can be prepared also from *β*-caryophyllene nitrosochloride. With hydrogen chloride *β*- and *γ*-caryophyllenes yield *caryophyllene dihydrochloride*, m.p. 69°–70°, whilst on hydration they give two tricyclic alcohols, *α*- and *β-caryophyllenic alcohols*, m.p. 117° and 96° respectively (Wallach and Walker, Annalen, 1892, 271, 288; Asahina and Tsukamoto, J. Pharm. Soc. Japan, 1922, 463).

From the products of the ozonolysis of the caryophyllenes (a mixture of the *α*-, *β*-, and *γ*-hydrocarbons) Semmler and Mayer (Ber. 1911, 44, 3657) isolated (i) a *ketone*, $C_{10}H_{16}O$, (ii) a *diketone*, $C_{12}H_{20}O_2$, (iii) a *diketo-aldehyde*, $C_{14}H_{22}O_3$, (iv) an *acid*, $C_8H_{14}O_2$, (v) a *keto-acid*, $C_{11}H_{18}O_3$, and (vi) a *diketo-acid*, $C_{14}H_{22}O_4$. Oxidation of the last two acids with nitric acid gave as an oil *caryophyllenic acid*, $C_9H_{14}O_4$. These observations have been confirmed by Ruzicka and Wind (*l.c.*), who have shown that the keto-acid, $C_{11}H_{18}O_3$, (*semicarbazone*, m.p. 183°), gave on oxidation with sodium hypobromite a dibasic acid, *homocaryophyllenic acid*, $C_{10}H_{16}O_4$, whilst in a similar manner a *keto-dibasic acid*, $C_{13}H_{20}O_5$, was prepared from the diketo-acid, $C_{14}H_{22}O_4$. This diketo acid on digestion with alkali undergoes ring closure with the formation of an unsaturated *keto-monobasic acid*, $C_{14}H_{20}O_3$, which contains a —COMe group. Interpretation of these results became possible when the structure of caryophyllenic had been determined.

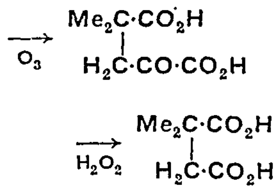
An examination of Semmler and Mayer's liquid acid by Evans, Ramage, and Simonsen (J.C.S. 1934, 1806) showed it to be a mixture of two crystalline acids, d-trans-*norcaryophyllenic acid*, m.p. 125°–127°, $[\alpha]_{5461}$ +137° (in chloroform), and d-trans-*caryophyllenic acid*, m.p. 80°–81°, $[\alpha]_{5461}$ +13·56° (in chloroform), *dianilide*, m.p. 282°, which can be converted into the d-cis-*acid*, m.p. 77°–78°, $[\alpha]_{5461}$ −7·4° (in chloroform), *dianilide*, m.p. 190° (Ramage and Simonsen, J.C.S. 1936, 746). By the reactions indicated below norcaryophyllenic acid has been shown to be represented by the structure (I) suggested by Ruzicka and Zimmermann (Helv. Chim. Acta, 1935, 18, 219).



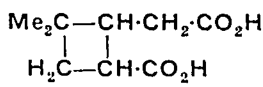
I.



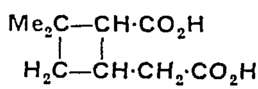
II.



The structure assigned to *d*-norcaryophyllenic acid has been confirmed by the synthesis by Rydon (J.C.S. 1936, 593) of *cis-dl*-norcaryophyllenic acid, m.p. 149°–150°, *anhydride*, m.p. 40°–41° (*dl-trans*-norcaryophyllenic acid, m.p. 148°–149°), from which *dehydronorcaryophyllenic acid* (II), m.p. 193°, identical with the acid prepared from *d-trans*-norcaryophyllenic acid, was obtained. Since caryophyllenic acid can be degraded to norcaryophyllenic acid (Ramage and Simonsen), it follows that it must be represented by either (III) or (IV):

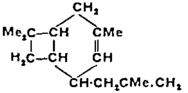


III.

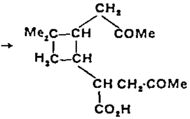


IV.

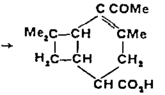
On the basis of these formulæ for caryophyllenic and norcaryophyllenic acids Ruzicka (J.S.C.I. 1935, 54, 509) and Ruzicka, Zimmermann, and Huber (Helv. Chim. Acta, 1936, 19, 343) have suggested that caryophyllene can be represented by (V), when the diketo-acid, $C_{14}H_{22}O_4$, will be (VI) and the dicyclic keto-acid, $C_{14}H_{20}O_3$, prepared therefrom would be (VII) or (VIII):



V.

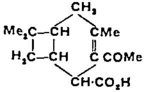


VI.



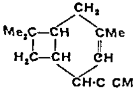
VII.

or

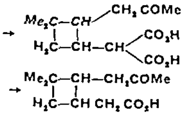


VIII.

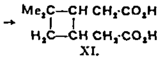
It is suggested further that the keto monobasic acid, $C_{11}H_{18}O_3$, which gives on oxidation with sodium hypobromite homocaryophyllenic acid, is derived from the isomeric hydrocarbon (IX) in accordance with the scheme.



IX.



X.



XI.

The structure (X) assigned to homocaryophyllenic acid has received support from the experiments of Ramage and Simonsen (J.C.S. 1937, 73).

These authors (J.C.S. 1936, 1581) have shown further that the caryophyllene represented by (V) is in all probability β caryophyllene. When the crystalline nitrosite of this hydrocarbon is degraded it yields mainly the acid (VI) together with a small quantity of (XI). The structure to be assigned to γ-caryophyllene remains undetermined.

By the dehydration of α-caryophyllenic alcohol a tricyclic hydrocarbon, *clovene*, b.p. 111°–113°/10 mm., d_4^{20} 0.924, n_D^{20} 1.4980, $[\alpha]_D$ +1.3° is obtained, whilst from β caryophyllenic alcohol iso*clovene*, b.p. 130°–131°/12 mm., d_4^{19} 0.943, n_D^{19} 1.5039, $[\alpha]_D$ −56.6° has been prepared. By the oxidation of clovene with chromic acid Ruzicka and Gibson (Helv. Chim. Acta, 1931, 14, 570) obtained a dicarboxylic acid, *clovenic acid*, $C_{15}H_{24}O_4$, m.p. 182°, which is extremely stable and has so far resisted all attempts to elucidate its structure (*cf.* Blair, J.C.S. 1935, 1927). J. L. S.

CASCARA SAGRADA, B.P.; U.S.P. The dried "sacred bark" of *Rhamnus Purshiana* DC., a small tree abundant in Northern California and the States of Washington and Oregon. Together with *R. californica* Eschscholz (which has a very similar action) it had long been known to the Indians as a cathartic; since about 1880 cascara has come into extensive use in American and European medicine as a laxative. The European species *R. cathartica* L., the Common Buckthorn, and *R. Frangula* L., the Alder Buckthorn, have been used for the same purpose. The older chemical literature concerning cascara is very conflicting, for a summary of which *see* Jowett (Rep. Amer. Pharm. Assoc. 1904, 1); he confirmed the presence of *emodin* together with a small proportion of the isomeric frangula-emodin of Thorpe and Miller (J.C.S. 1893, 61, 6). The literature since 1904 is summarised by Hoch (Amer. J. Pharm. 1933, 105, 64; 39 items). Hoch agrees with Hauser (Pharm. Acta Helv. 1931, 6, 79) that the glucosides present are rhamnosides of the anthranols of chrysophanic acid, frangula emodin monomethyl ether and cascarol. The changes taking place during storage of the bark (1 year is prescribed by some pharmacopœias) probably involve oxidation of the anthranol to anthraquinone rhamnosides, with some hydrolysis. The anthraquinone derivatives increase during storage. "Although most likely an integral part of the purgative complex, the anthraquinone derivatives have no cathartic properties." The most important principle of cascara is unknown. It would seem that this principle is contained in *peristaltin Ciba*, according to Tschirch and Monikowski (Arch. Pharm. 1912, 250, 92), a yellowish amorphous powder, readily soluble in water, and active also when injected; it contains rhamnosides of chrysophanic acid, emodin methyl ether, and *cascarol*, $C_{11}H_{10}O_5$, yellow needles, m.p. 218°, but no free hydroxy methyl anthraquinones. The chemistry of *R. Purshiana* and *R. Frangula*

is more particularly dealt with by Tschirch and Pool (Arch. Pharm. 1908, **246**, 316). Various assay methods, based on the colorimetry of emodin, are futile, according to Hoch, since there is no evidence that the emodin content can be correlated with therapeutic activity (*e.g.* Morrison, J. Amer. Pharm. Assoc. 1931, **20**, 1276). For tests on the human subject, *see* Hoch, for animal tests Gruber, Bryan, and Richardson (J. Pharm. Exp. Ther. 1932, **44**, 479).

Cascara bark contains about 2% of fat, a substance *rhamnol*, $C_{20}H_{36}O$, m.p. 132°–133°, and a small proportion of a volatile oil (Jermstad, J. Pharm. Chim. 1933, [viii], **17**, 76; Pharm. Acta Helv. 1929, **4**, 90). For differential tests of Cascara and *Rhamnus Frangula*, *see* Kroeber (Schweiz. Woch. Chem. Pharm. 1910, **48** 377); Beal and Okey (J. Amer. Chem. Soc. 1917, **39**, 716). G. B.

CASCARILLA, ESSENTIAL OIL OF. The oil distilled from the bark of *Croton Eluteria*, Bennett (Fam. Euphorbiaceæ), which is indigenous to the Bahama Islands and also grown in Honduras. Yield 1–3%.

Constituents.—Cymene, *l*-limonene, eugenol, cresol, sesquiterpenes, aldehydes, and esters of cascarillic acid with traces of palmitic and stearic acids. Cascarillic acid is isomeric with undecylic acid.

Characters.—A pale yellow oil, sp.gr. at 15° 0·896–0·925, a_D^{20} + 4° to + 10°, n_D^{20} 1·489–1·496. Initial saponification value 4–8, after acetylation, 60–70. C. T. B.

CASEIN. (Caseinogen.) Casein is a phosphoprotein found in the milk of mammals. It is the principal protein of cow's milk, which is its chief commercial source. It is amphoteric, and occurs in milk as a colloidal suspension, probably a complex with dicalcium phosphate (J. Brigando, Lait, 1933, **13**, 661). Together with the fat, it can be separated by ultrafiltration, the lactose, mineral salts, and soluble albumen remaining in the ultra-filtrate.

Many American and some English authors have preferred to use the term *casein* for the commercial product produced by precipitation from milk, and the word *caseinogen* for the protein (non-coagulable by heat) of milk in its natural condition, or when precipitated under the special laboratory conditions referred to below. In view of the doubt whether the latter term refers to a single specific chemical compound, and of the fact that there are two quite distinct types of the commercial product, the term *casein* is used in both senses throughout this article.

PREPARATION OF PURE CASEIN.—Pure casein is prepared by acid precipitation of separated milk. Most of the recent research work has been carried out with casein prepared by one of the following methods:

Hammarsten method ("Handbuch der biochemischen Arbeitsmethoden," E. Abderhalden, Berlin und Wien, 1910, Vol. II, p. 384).—Separated milk is diluted with 4 vols. of cold water and dilute acetic acid (1:100) is added with continuous mixing until the casein has precipitated. The latter is washed several times with water, first by decantation and then centrifuging. The moist casein is then dissolved in dilute ammonia, agitating during the addition, and care being taken that the p_H value does not exceed 7·0. The solution is filtered or centrifuged and the casein reprecipitated by the addition of the calculated amount of acetic acid. The precipitated casein is washed with water, redissolved in ammonia, and reprecipitated with acetic acid. The precipitate is finally washed several times with water.

Van Slyke and Baker Method (J. Biol. Chem. 1918, **35**, 127).—Separated milk is not diluted in this method, and normal lactic acid or a mixture of 1 part of normal hydrochloric acid and 1 or 2 parts of normal acetic acid is preferred to acetic acid alone. The acid is gradually introduced beneath the surface of the milk, which is efficiently agitated. The addition of the acid is carefully controlled by withdrawing small samples of the mixture, adding an equal volume of water, and centrifuging. At the coagulation point the whole of the casein is thrown down on centrifuging. The casein is washed by agitating with water, allowing to stand, and centrifuging. This is repeated several times, but the casein is not redissolved in alkali as in the older method. The last traces of phosphate are removed by electrolysis of the casein suspended in dilute acetic acid at p_H 4·7. It is claimed that casein can be purified to an ash content of 0·069% by electro-dialysis (A. L. Elder *et al.*, Ind. Eng. Chem. [Anal.], 1934, **6**, 65).

The casein prepared by either of the above methods is finally extracted with 70–80% alcohol, ether, and high-boiling petroleum or benzene or toluene in a continuous extractor.

Properties.—Pure casein, prepared by acid precipitation, is a white amorphous powder, without taste or odour. It is practically insoluble in water and quite insoluble in most organic solvents. It is readily dissolved by alkalis, forming acid and neutral salts, and can be precipitated unchanged by the addition of acids. It swells in contact with dilute hydrochloric acid, and may be partially dissolved, the amount going into solution being dependent on the p_H of the acid. The isoelectric point of pure casein is usually regarded as falling at p_H 4·6 but certain physico-chemical measurements have indicated either that this value is not strictly correct or that there is an isolectric zone (C. La Rotonda, Annali Chim. Appl. 1929, **19**, 310; E. B. R. Prideaux and F. O. Howitt, Proc. Roy. Soc. 1929, A, **126**, 126).

In dilute alkaline solutions casein has a lævo-rotatory action on polarised light.

Casein absorbs hydrogen chloride with the formation of definite compounds. It gives a violet coloration when dissolved in concentrated hydrochloric acid.

Much work has been done on the question whether casein, as above described, is a homogeneous substance, and the bulk of the evidence suggests that it is not. Probably the differences recorded by various investigators were due to the extent to which they had purified their casein. J. Gróh, E. Kardos, K. Dénes and V. Serényi (Z. physiol. Chem. 1934, **226**, 32)

have isolated two fractions, differing in their tyrosine and tryptophan content and in their rotation. They have obtained these fractions by three different fractional precipitation methods, irrespective of the method, and have found that a mixture of the two was identical with the product obtained by complete precipitation.

By ultra-centrifugal methods T. Svedberg, L. M. Carpenter and D. C Carpenter (J. Amer Chem. Soc. 1930, 52, 241, 701) have concluded that neither of the above methods of preparation gives a single protein, but mixtures of proteins of different molecular weights. From Hammarsten casein they isolated what was probably a pure substance of molecular weight 375,000±11,000, in phosphate buffer solution of p_H 6·8, whilst they concluded that the bulk of the casein obtained by the Van Slyke and Baker method has a molecular weight between 75,000 and 100,000. Serological studies (Carpenter and Hucker, J. Infect. Dis. 1930, 47, 435) showed these proteins to be definitely distinct. Analytically, D. C. Carpenter (J. Amer. Chem. Soc. 1931, 53, 1812–1826) concluded that casein obtained by the Van Slyke and Baker method consists largely of proteins of a molecular weight 98,000. The osmotic pressure measurements of N. F. Burk and D. M. Greenberg (J. Biol Chem. 1930, 87, 197) indicate an even lower value for the molecular weight, 33,600±250. Other studies on the fractionation of Hammarsten casein have been made by B. Jirgensons (Biochem. Z. 1934, 268, 414) (*See also* A. D Robinson *et al.*, J. Phys. Chem. 1932, 36, 1858.)

There is distinct evidence of slight structural differences in casein from different sources (*e g.* differentiation of Indian buffalo milk casein and English cow casein, R. B. Gode and D. L. Sahasrabuddhe, J. Central Bureau Animal Husbandry and Dairying, India, 1929, 3, 10, 33). A. F. Anderson (Amer. J. Dis. Children, 1932, 44, 178) concluded that there is a lack of species specificity in the caseins obtained from cow, goat and human milks, but chemical differences were indicated (*see also* M. L Demanez, Compt. rend. Soc. Biol. 1933, 112, 1560, 1561).

The probable percentage composition of casein is: C, 53 50; H, 7·13; N, 15 80; P, 0 71, S, 0 72; O, 22 14. (Van Slyke and Bosworth J. Biol. Chem. 1913, 14, 203).

Manufacture of Industrial Casein.—Although other sources have been described (*e g.* vegetable, such as soya bean or peanut cake) practically the whole of the casein of commerce is prepared from cow's milk. The methods employed can be grouped under two headings, viz. acid precipitation and rennet precipitation. The resultant products show marked differences in properties and find different applications in industry.

There are two main modifications of the acid precipitation method:

(1) Precipitation by the direct addition of an acid, usually hydrochloric or sulphuric.
(2) Precipitation by lactic acid formed by bacterial action from the lactose present in the milk ("self souring" method).

Precipitation by mineral acids found wide application during the war, when speed was a primary consideration, and when it was not always practicable to take all the precautions necessary for the preparation of satisfactory "self-soured" casein. Mineral acid precipitation is extensively used in the United States, but the "self-souring" method is more generally practised in other parts of the world.

Milk for casein manufacture should be efficiently separated and should not contain more than 0·1% of fat. Not only does inadequate separation mean waste of fat, but the presence of excessive quantities (*e.g.* more than 1–1½% in rennet caseins or 2–3½% in acid caseins) will affect its commercial value. The milk must not have been pasteurised at too high a temperature, otherwise insoluble denatured lactalbumin will be present. Milk from cows shortly after calving is unsuitable, as the colostrum present gives rise to a soft curd from which it is almost impossible to remove the water.

Plant used for casein manufacture varies extensively, but acid-resistant precipitation tanks (wood or metal) are to be preferred, since iron contamination discolours the casein and may render it unfit for some purposes.

Precipitation by Mineral Acids.—According to the older practice, fresh separated milk was heated to 120°–125°F. for sulphuric acid precipitation (5° lower if hydrochloric acid was to be used), and there was added about a pint of commercial sulphuric acid (sp gr. 1 83) diluted with 2 quarts of water, or 2¼ pints of commercial hydrochloric acid with an equal volume of water for each 100 gallons of separated milk.

After precipitation of the curd, the whey was drained off, the residue cooked at 170°–180°F., washed, pressed, and dried at 110°–115°F., care being taken to avoid overheating on the one hand or too slow drying on the other.

A much improved product is obtained by the "grain curd" method, various modifications of which are described. In this method precipitation is effected at a lower temperature and the curd is not cooked. In one satisfactory method (C. S. Trimble and R. W. Bell, Creamery and Milk Plant Monthly, 1930, 19, No 8, 40–44), hydrochloric acid, diluted with 8 parts of water, is slowly added to fresh separated milk at 94°–96°F. with rapid stirring. Sufficient acid to produce a p_H of 4·1 (equivalent to 0 5% of lactic acid) is used. After the whey has been drained off the curd is washed two or three times with water at 94°F., pressed, milled, and dried at 125°–130°F. The highest grades of casein can only be produced if the p_H of precipitation is carefully controlled. Another method for which a high degree of efficiency is claimed has been worked out by F. L. Chappell, N.Y. (Richard W. Smith, Ind. Eng. Chem. 1934, 26, 819). An ingenious arrangement is employed to secure, practically instantaneously, intimate mixing of the hydrochloric acid (sp gr. 1 20 diluted with four times its volume of water) and the skimmed milk (preheated to 110°F.). (*See also* G. Genin, Lait, 1935, 15, 251)

Preparation by "Self-souring"—To well

separated milk "starter" is added in the proportion of about ½ gallon to every 100 gallons of milk. The whole is well mixed, the temperature adjusted to 80°F., and allowed to stand usually overnight, until a p_H of 4·6 has developed. The curd is then cut up with specially designed knives and the temperature is gradually raised until 120°–140°F. is reached after 40–50 minutes. The curd is held at this temperature for 20 minutes before the whey is drawn off; it is then washed with hot water, pressed, and dried.

Rennet Precipitation.—High quality rennet casein can only be made from efficiently separated milk in which acidity has not been allowed to develop. The amount of rennet required will depend both on the temperature and on the acidity of the milk, decreasing as either increases. Different preparations of rennet vary in acitivity. If the acidity of the milk be 20° (*i.e.* if 20 ml. of $N/10$ caustic soda are required to neutralise the acid in 100 ml.), about 1½ oz. of rennet should curdle 100 gallons of milk. The rennet is diluted with water and is stirred into the milk at about 95°F. The milk is allowed to "set" undisturbed, *i.e.* for 20–30 minutes, and the curd is cut with special knives. The mass is then agitated, gently at first, and then more vigorously, whilst the temperature is raised to 150°F., about 1 hour being taken in the process. Considerable skill needs to be exercised during this cooking process or "cheddaring" (*i.e.* the formation of tough rubber-like agglomerates) will occur. The curd is then allowed to settle and the whey drawn off. The casein is washed, pressed, and dried as before described. The mechanism of rennet precipitation has been extensively studied by Ch. Porcher in several papers in Lait, 1930 and 1931.

Caseins having physical properties intermediate between those of rennet and acid or lactic caseins are sometimes prepared by allowing the acidity to develop, as in the "self-souring" process, and then, before a p_H of 4·6 has been reached, precipitating with rennet.

Curdling by Electricity.—Various methods of precipitating casein by electricity have been described, but, as far as is known, none is commercially employed. In general they can be classed as modifications of the acid precipitation method, rather than true applications of electrophoresis, as precipitation is said to be due to the phosphoric acid liberated by the electrolysis of the phosphates present. A method of obtaining casein and lactose by electro-dialysis is described by G. Jiro Kato (J. Soc. Chem. Ind. Japan, 1933, 36, 158B).

Drying the Curd.—Various devices have been described, but the most important points are the avoidance of local overheating, causing darkening, and of too slow drying, when the casein may become sour and mouldy. The temperature must be carefully controlled. The simplest drier is a tunnel, through which trays of casein move in the opposite direction to a draught of warm air. Other devices employ a heated cylinder which is rotated to keep the casein in motion.

PROPERTIES OF COMMERCIAL CASEIN.—Rennet casein should be clearly distinguished from acid or lactic casein, since they are used for totally dissimilar purposes. The former is almost invariably sold in the unground state, whilst the latter may be unground or ground to various degrees of fineness up to 120 mesh. The colour is best judged from the unground material. High-grade rennet casein is practically white, whilst unground lactic casein has a pale yellowish tint. Both should be free from dirt and dark particles.

Some differences between acid and rennet casein are given in the papers of H. Courtney Bryson mentioned below (*see also* C. A. Cooper and P. G. T. Hand on the determination of p_H of rennet casein, J.S.C.I. 1936, 55, 341T).

The following table gives typical analyses of commercial casein :

	Rennet.	Lactic.
Protein ($N \times 6{\cdot}38$) . .	78·0%	85·0%
Fat	1·0%	2·5%
"Ash"	8·0%	1·0%
Moisture	11·5%	10·5%

It will be seen that the "ash" is much higher in the case of rennet casein. Rennet casein differs from acid casein chiefly in its solubility in alkalis. Acid casein is readily soluble in the hydroxides, carbonates, bicarbonates, sulphites, borates, etc., of the alkaline metals. Rennet casein is insoluble in sodium carbonate and bicarbonate, and is only partly soluble in borax and ammonia. It is soluble in trisodium phosphate. Both acid and rennet casein are soluble in alkaline earth hydroxides, but the insoluble caseinates are speedily precipitated if an excess of alkali be present.

Acid casein is readily soluble in cold alkali hydroxides, but with the other alkalis it dissolves only slowly and warming is usually practised. The easiest way to prepare a solution without obtaining lumps is to mix the casein and alkali solution in the cold, stirring vigorously whilst doing so, and then to allow the mixture to stand for about 15 minutes. The temperature is then raised to 130°–140°F., and the mixture stirred until the casein has completely dissolved, about 10 minutes usually being required.

According to E. Sutermeister ("Casein and its Industrial Applications," New York, 1927) the quantities of alkalis required to dissolve 100 parts of casein are :

$NaOH$	3·95
NH_4OH	3·15
$Na_2B_4O_7,10H_2O$	14·70
$Na_3PO_4,12H_2O$	12·30
$Na_2SO_3,7H_2O$	14·00
Na_2CO_3	5·14

The solutions of casein in alkalis are not coagulated by heating but are precipitated by acids and by many metallic salts. In the former case, the casein is thrown down unchanged. The stability of alkali casein solutions depends on the p_H value. Even with quite low p_H values slow hydrolysis occurs, and the physical constants show a change within about 24 hours. Hydrolysis is more rapid with more

alkaline solutions. Formaldehyde forms with casein a highly insoluble compound, and this property finds wide application in industry.

The viscosity of different samples of commercial casein, dissolved in alkali according to the same formula, varies considerably, and is of great importance in the industrial use of casein. The subject is distinctly complicated, but viscosity appears to depend, amongst other factors, on the previous history of the casein, the p_H of the solution, and the age of the latter. Some interesting studies on the viscosity of casein by H. Courtney Bryson occur in British Plastics, 1932, 3, 510, 512, 514, 567. The extent to which alkaline solutions will froth is also a variable property of importance to the user, especially in the paper industry. It is probable that frothing is connected with slight decomposition of the casein rather than with gross causes such as the amount of undissolved matter present, as was once believed (*v. infra* Casein in the Paper Manufacturing Industries, p. 415).

The "ash" is a determination to which many users attach considerable importance, but the calcium content is a much more reliable figure, as the "ash" can be made to vary widely according to the method of ashing. Consideration is also given to the moisture, to the fat as determined by a modified Werner Schmidt method, and to the nitrogen. The amount of matter insoluble in alkali is a good indication of quality and is often included in specifications. Reference to methods of analysis will be found in Jephcott and Ratcliffe (Proc. Intern. Dairy Cong. 1925, II, 1271); Ulex (Chem. Ztg. 1925, 49, 3074; 1930, 54, 421); Marcusson and Picard (Mitt. Materialpruf., 1927, 5, 122; 1927, B, 890); Paper Trade J. 1932, 94, T.A.P.P.I. Sect. 268, B, 748; and various papers in Lait, for 1928, 1929, 1932, and 1934.

USES OF CASEIN.—The chief sources of supply of rennet casein are France and New Zealand, of lactic casein, Argentine, France and New Zealand, smaller amounts being made in India and European countries. Imports from the Argentine probably exceed those from France and New Zealand combined, but the former are generally inferior to the latter.

The industrial applications of casein are manifold, and it is impossible to enumerate them all in this article. On the one hand is the large field of casein plastics (*q.v.*), and on the other are applications more or less linked with the adhesive properties of casein, viz. glues and cements, paints and distempers, paper and cardboard making, leather finishing and calico printing, etc. The fields merge into one another at numerous points. Casein is an excellent emulsifying agent and is used in both medicine and industry for that purpose. Finally, casein is widely used in food preparations and in medicines.

Rennet casein is almost exclusively used in the manufacture of plastics, whilst acid casein is chiefly employed in the other fields mentioned.

ALIMENTARY CASEIN.—The term "alimentary casein" is very loosely used in the industry, and whilst some consider its use properly to be restricted to casein precipitated with acetic acid, it often refers simply to finely ground, high grade lactic casein.

The use of casein as a food material is dependent on its high protein content and to the presence of phosphorus. Owing to its insolubility, it is rarely employed as such, but as one or other of the soluble caseinates. Caseinates are used in a number of proprietary diabetic and invalid food preparations. Most of these are a loose combination of casein with 5% sodium glycerophosphate. Calcium and sodium caseinates have a limited use in infant feeding.

Casein has been used as a food adulterant and as a constituent of egg and other "substitutes."

Casein as a constituent of cheese is outside the scope of this article, but mention may be made of the use of casein in the manufacture of certain soft cheeses, particularly in Germany, where a proportion of casein is sometimes incorporated with fresh curd, dependent partly on local taste and partly on the economic conditions prevailing. Casein for this purpose must have been prepared with exceptional care, for the presence of extremely small traces of iron causes darkening of the cheese as it "ripens."

CASEIN IN MEDICINE.—In addition to its use as an emulsifying agent in the preparation of emulsions and ointments, colloidal suspensions of the caseinates of the heavy metals have been employed.

Additive compounds with iodine (*e.g.* Iodo Casein N.N.R. Amer. Med. Assoc.) have been widely used as an easy method of administering this element.

Preparations containing casein formaldehyde and casein tannic acid compounds have been employed, the former as a protective covering for wounds and the latter as a means of administering tannic acid.

CASEIN GLUES.—Considerable antiquity is claimed for casein glues or cements, but they have come into greater prominence during recent years. They were used extensively in aircraft manufacture during the war, and now find wide application in the plywood and veneer industry (*cf.* B.S.S. Casein Cement, 3V 2).

Adhesives consisting simply of solutions of casein in caustic soda, borax, or ammonia are not usually employed for woodwork, but are widely used in the manufacture of cardboard, paper tubes, etc., and, in a totally different field, in the manufacture of double cloths.

The basis of most casein adhesives is lime, and the waterproof qualities are usually due to the conversion of the casein into insoluble calcium caseinate after glueing. The term "waterproof" is rather a misnomer, as no casein glue is fully waterproof. "Water resistant" would be a better term.

A moderately strong glue is given by a formula of the type of:

Casein	7.5 parts
Slaked lime	1.5 „
Caustic soda	1.0 „
Water	30 „

The presence of free caustic soda is a disadvantage.

Lime alone, *e.g.*:

Casein	10 parts
Slaked lime	2 „
Water	40 „

gives a strong glue, with high waterproof qualities, but such a glue has only a short working life and must be used within about half an hour of mixing with water.

By far the most popular type is that employing lime and a sodium salt, with which it forms a precipitate. Numerous salts have been used, but sodium fluoride has a well-deserved popularity. If the ratio of lime to sodium fluoride is increased, the waterproof qualities are greater but the working life is shorter, and the exact adjustment is a matter for the consideration of the user.

Casein glues containing lime and sodium silicate have been used.

Whilst many glues are marketed as powders, requiring only admixture with cold water before use, it is advantageous, if the glue is to be prepared from its components, to soak the casein first in some of the water and then to add the other ingredients dissolved or suspended in the rest of the water, stirring until the mixture is homogeneous. By this method the danger of lump formation is minimised.

The testing of casein glues is a complicated subject, into which many factors enter. Insignificant variations in the wood of the test-pieces have a big effect on the results. The length of time which elapses between the mixture of the glue with water and its application to the wood has a great influence on the strength of the joint.

The use of formaldehyde in the manufacture of waterproof glues has been described but has not found wide application.

An enormous number of patents have had as a basis the admixture of inert substances, such as cork, rubber latex, or asbestos, with a casein glue for the preparation of agglomerates.

Casein Paints and Distempers.—Casein has for many years found an extensive application in paints and distempers. Casein paints have the advantages of cheapness and, as they can be sold in the dry form requiring only admixture with water, of convenience over oil paints, whilst they are more easily and efficiently waterproofed than paints containing glue or dextrin. The widest use of casein in this industry is in the preparation of washable exterior paints. These comprise an alkaline solution of casein as "binder," an inert substance such as whiting as "covering," various pigments (which, of course, must be fast to alkalis), and lime to convert the casein into insoluble calcium caseinate and thus to confer washable properties. Other substances, such as formaldehyde and hexamethylenetetramine, have been used for the latter purpose, but, for cheapness and simplicity, lime is preferred. The quantity of lime must be carefully chosen. Too little affects the stability and the waterproof qualities adversely, whilst too much causes premature precipitation and the paint to flake off.

Suitable pigments are:

For white:	Whiting, china clay, zinc oxide.
„ yellow:	Ocre, hansa yellow, naphthol yellow, chrome yellow.
„ brown:	Umber, sienna.
„ black:	Carbon blacks.
„ red:	Oxides, lithol red.
„ blue:	Ultramarine.
„ green:	Green earth, ultramarine green, lime green.

A general article on casein paints appears in Ind. Chem. 1932, **8**, 146 (H. Courtney Bryson), from which the following simple typical formula is taken:

Casein	10 parts
Lime	12 „
Chalk	60 „
Clay	10 „
Pigments	8 „

Glycerol or glucose can be added to prevent cracking and to ensure adhesion (*see also* Kurt Beck, Gelatine, Leim, Klebstoffe, 1934, **2**, 173).

Alkaline solutions of casein are used sometimes as "binders" in ordinary non-washable distempers, but glue is more often employed. They are also sometimes used with oils, replacing some 25–50% of the water, and the resulting paint is very satisfactory for outdoor work. Fireproof paints frequently include phosphates or silicates. Another class of casein paint is one including rubber latex. A washable paint for paper (*e.g.* wallpaper), cloth, or leather is prepared by mixing an ammonia solution of casein with glycerin and formaldehyde.

Casein in the Paper Manufacturing Industry.—A very important application of lactic casein is in the paper-making industry, especially in the manufacture of high-grade surfaces, such as art papers. It is successfully competing with bone-glue and starch, over which it has the advantage of being more easily made waterproof. The casein itself must be of a high quality, free from insoluble matter, and with no tendency to froth under the conditions of use.

A solution of casein is prepared, usually with two or more alkalis, the choice of alkalis being dependent upon the paper stock and type of machine used by the individual manufacturer. The corrosive nature of caustic soda rather counterbalances its cheapness. Borax cannot be used with satin white. Ammonia is very popular, as any excess dries off and the coating is to a certain degree waterproof.

The casein solution is mixed with various mineral matters, such as satin white, precipitated chalk, china clay, or blanc fixe. The proportions will depend not only on the choice of mineral matter, but also on the coating technique (*see* Mich. Eng. Exp. Sta. Bull. 1932, No. 42, 3). The physical properties must be such that the mixture spreads evenly without leaving brush marks. Suitable pigments may also be incorporated.

Coatings may be waterproofed by subsequent treatment with solutions of salts of heavy metals, which precipitate insoluble caseinates, but most of these are coloured and are consequently

limited in their application. Formaldehyde has also been used for the purpose. It may be used in relatively small quantities so that the coating mixture can be applied before appreciable precipitation has occurred, or else in the form of hexamethylenetetramine, which is subsequently decomposed by heat.

Casein has found other applications in the paper-manufacturing industry, in particular in speciality papers. It has been used both in place of, and in conjunction with, resin in sizing

Attempts to correlate the results of laboratory analysis and coating quality have met with mixed success. On this subject notice should be taken of an important paper by E. O Whittier, S. P. Gould, R. W. Bell, M B. Shaw, and G W. Bicking (Ind. Eng Chem 1933, 25, 904) A standardised technique for the determination of frothing has been developed by C. W. Richards and L. W. McFail (Paper Trade J. 1933, 97, T.A P.P.I. Sec 1) Anti-frothing agents, some of a proprietary nature (*e g.* "Rubberine Gel," *see* Werner Esch, Gelatine, Leim, Klebstoffe, 1934, 2, 51), have found employment.

CASEIN IN THE MANUFACTURE OF ARTIFICIAL WOOL.—The manufacture of artificial wool from casein is being developed in Italy. This new process, which has been patented, is the outcome of the researches of A Ferretti The details have so far been kept secret by the patentees and by the Italian Company, Snia Viscosa, operating the patents, so that little information is available to the public The general principles have been discussed in an article by G. May in Lait, February, 1936 (*cf* Ind. Chem. 1937, 13, 186) It is there stated that mineral acid casein, or casein curd, is dissolved in a solution of alkali or an alkaline salt. The casein solution is forced through a metal plate pierced by numerous fine perforations, and the extruded liquid enters a suitable coagulating bath, resulting in the formation of fibres of casein, which are then removed and dried. The dried fibres have an appearance and properties similar to those of natural wool It is stated that a given weight of casein will yield approximately a like weight of artificial wool The new product is being marketed under the trade name "Lanital." The process is being operated on a semicommercial scale in Italy, and if the claims that have been made for quality of product and low manufacturing costs are substantiated, it would seem that this new development may have notable repercussions on the wool and casein industries.

MISCELLANEOUS USES.—The literature and patent specifications contain many suggestions of ways in which casein can be or has been used, *e g.* for the sealing of bottles, the refining of wines, the making of films, and in the textile industries—in the last-named both in connection with calico printing and with the waterproofing of materials. Many of these appear to be simply special and ingenious applications of the general principles already described, and none of them has had any considerable industrial use.

For further references, *see* Science Library Bibliography, No. 327 (1937). H. J.

CASEIN PLASTICS. *History of the Industry*—About the year 1897, W. Krische, a printer in Hanover, evolved the idea of coating white cardboard with a solution of casein, thus producing a film which he intended to harden, and to render waterproof by subsequent chemical treatment.

At the same time Adolph Spitteler, of Prien in Bavaria, was working upon the problem of waterproofing casein. As the result of a collaboration these two workers discovered the formaldehyde-casein reaction, on which the whole industry is based.

They found that formaldehyde forms more or less stable compounds with casein, altering its properties appreciably. They noted that solubility in water and capacity for hydration had been lost, and further, that the compound produced was insoluble in acid. An English patent was taken out in October, 1897, and they then devoted their energies to the exploitation of this discovery. They worked more on the idea of producing plastic materials in the form of masses, rather than as protective coatings.

The process was finally taken up by the Galalith Company of Harburg, and developed by them as a commercial proposition.

The history of the development of the industry in this country is also interesting. In 1909 a Russian student, Victor Schutze of Riga, patented a process for the manufacture of solid plastic material from milk curds. This process was bought by an English company, and a plant was erected to work it.

The process as patented by Schutze was found to be impracticable, being based on what is known as the wet process. The English company had therefore to work out quite independently a modification of this process This was done successfully and the process so worked out is now known as the dry process and is universally adopted as the standard method

Dry Process.—The process is substantially as follows :

The casein is treated by means of heat and pressure with the minimum quantity of water to effect its flow during the process of manufacture. Rennet casein is used exclusively in the production of casein plastics, and the dry rennet casein is ground to pass a 40-in. mesh. It is important to note that the temperature of the casein is kept as low as possible during the process of grinding, otherwise discoloration of the casein will result.

The type of mill usually used for this grinding is the flour mill type, in which the material passes between finely corrugated steel rollers

Sixty kg. of the ground casein is considered a standard charge for an operation. The charge is placed in a suitable mixer, and any dry pigments which have to be added are mixed in at this stage.

The colours are produced mostly by the addition of acid dyestuffs. The dye is dissolved in a definite proportion of water and sprayed on to the mixing ; the mixing is then further continued until a uniform distribution of the dye solution takes place throughout the mass The mixing machines which are used for this process are of the dough mixing type.

The dyed powder is now fed to extruding machines. These machines are of the same type as are used in the rubber industry. They are modified in various ways to meet particular requirements, and consist of a jacketed worm arranged so that complete temperature control can be obtained either by steam or water circulation.

They are fitted at one end with a nozzle which has various screens inserted to control the flow of the material as it passes through the machine.

The screw plasticises the dyed powder as it comes forward to the nozzle ; the screens put up a resistance, and assist in the production of a thoroughly homogeneous product. The material as it now leaves the nozzle of the machine is in a soft and rubbery condition.

Mottled colours are produced by mixing the feed powder with nibs of the complimentary colour or colours required. The nibs are made by extruding through another machine rods of about 4 mm. diameter. These thin rods are cut up by chopping machines into 4 mm. lengths. Such small pieces are known technically as nibs. The fact that these nibs have passed through the machine ensures a preliminary plasticising caused by the action of the screw. When they are now mixed with the base powder and again fed in the mixture to the machine, they are obviously harder and tougher than the base powder and thus stand out in relief to form the required pattern and colour.

The plastic material extruded by the machine is made in the form of rods, ribbons, or tubes as may be required. If sheets are being manufactured, the ribbons or rods are cut to a definite length, weighed off according to the thickness of the sheet required, and placed in a steel mould. The moulds are then placed in a hydraulic press and the material is subjected to heat and pressure. The final pressure may range from 150 to 200 tons on the platen.

The material is cooled before removing from the mould. At this stage it will be found to be still in a soft and somewhat rubbery condition, but it is sufficiently rigid to stand upright in racks.

These racks containing the casein sheets then pass into the formaldehyde tanks, where a prolonged treatment in a 4–5% solution of formaldehyde is given. The thickness of the material, of course, determines the length of time that the sheets have to be immersed, and this treatment may vary from 10 days to 10 weeks.

The sheets then pass from the tanks to the drying room and are dried out in a plentiful supply of air, the temperature being kept round about 27°–30°C. During this drying the sheets may warp considerably, and they have to be finally straightened. This is done in hydraulic presses. They are softened by dry heat first of all and then pressed out. After this final straightening they remain rigid and are ready for the market. The size of the sheet which is manufactured is usually 20 in. × 16 in.

To return to the extruding machine, the material which has to be made into rods is cut off in 30 or 40 in. lengths, cooled, and placed in trays. If tubes are required, the nozzle of the extruding machine is fitted with a screen which carries centrally a pin. This pin passes through the nozzle and may project slightly at its mouth. The material flows round the pin and so forms the required tube.

The tubes and rods are placed in trays and then pass into the formaldehyde tanks, where they remain until complete formalising takes place. The circulation of the formalin in the tanks is of the utmost importance, as is also an accurate temperature control. Both these factors have a definite bearing on the length of time required in the formalising process.

When the rods and tubes are completely formalised, they are dried in rotating drums through which hot air is passed. They come out of the drums at the end of the drying process perfectly straight. This finishes the actual manufacturing process.

Further treatment of the material, such as sanding the sheet to a smooth surface, trapping the rods (which is a process of central grinding) to accurate dimensions, and finally polishing, both sheets and rods, are more in the nature of finishing operations than actual manufacture.

Properties of the Material.—The specific gravity of the casein plastic material is 1·33–1·34; age and atmospheric conditions may cause a variation in the figure ranging over ½% either way.

Action under Heat.—At 130°C. the material begins to discolour, but the change is very slight and is only a disadvantage in the more delicate colours. At 160°C. the discoloration shows in all colours, but the material still retains its plastic and cohesive nature. At 200°C. after some minutes disintegration takes place.

The material is non-inflammable and will only burn on being held in a flame. It is somewhat hygroscopic and can be softened in hot water, moulded, and pressure polished.

It is an excellent insulator and can be used for all low-tension work, but on account of its hygroscopic properties it is not suitable for high-tension work or for outdoor work of any description.

In most respects it is worked like horn and ivory; it can be turned, drilled, polished, stamped, moulded and engraved.

Altogether it has found its way into thirty or forty trades, and it is now looked upon as a thoroughly reliable and proved material. It is a beautiful material to handle and can be used in the production of the most delicate pastel shades as well as for rich and decorative colour schemes. On this account and also on account of its relatively low production cost, the material is very popular in the world of decorative art.

R. D.

CASEIN WOOL, LANITAL *v.* CASEIN, *Casein in the Manufacture of Artificial Wool* (p. 416).

CASHEW APPLE, CASHEW NUT *v.* ANACARDIUM NUT.

CASHEW NUT SHELL OIL *v.* ANACARDIUM NUT.

CASIMIROEDINE *v.* CASIMIROINE.

CASIMIROINE and CASIMIROEDINE occur in *Casimiroa edulis* (Fam. Rutaceæ) which is a tree widely distributed throughout Mexico and Central America. It is known in Mexico as "Chochitzapotl" and "Iztactzapotl," and in Guatemala as "Matosano," in the Pharmacopœia

of Mexico the fruit and seed are called "Zapote blanco." Power and Callan (J.C.S. 1911, 99, 1993). The two bases are extracted from the kernels by hot alcohol.

Casimiroine (I), $C_{24}H_{20}O_8N_2$, m p. 196°–197° (from EtOH or CH_3COOEt) optically inactive, contains two methoxyl groups. Its salts dissociate in H_2O; *picrate* (needles, m p 165°) and *chloroaurate* (needles, m p 195°–196°) are the only two crystalline salts. For colour reactions, *cf* Power (*l c*). By boiling (I) with alcoholic potash CO_2 is split off, and by addition of 1 mol. of water *casimiroitine*, $C_{23}H_{22}O_7N_2$, m.p 171°, is formed By extracting the mother liquor of (I) with ammonia, *casimiroedine* (II), $C_{17}H_{24}O_5N_2$, m p. 222°–223° (from EtOH) is obtained. (II) is a fairly strong base, $[\alpha]_D$ −36·5°, insoluble in the usual organic solvents except hot EtOH, it does not contain methoxyl-groups, it gives a crystalline *chloroaurate*, m p 145°–148°. There is nothing further known about the constitution of the two bases. Both alkaloids are physiologically inactive. For other compounds, isolated from the kernels of *C. edulis cf.* Power (*l c*).

Schl.

CASSAVA. Two species are met with, *viz.* bitter cassava (*Manihot utilissima*, Pohl) and sweet cassava (*M. palmata* Muell., *M. Aipi* Pohl, or *M. dulcis*, var *Aipi* Pax). The fleshy roots contain large proportions of starch and after pulping and drying on hot plates yield *the tapioca of commerce.* The purified un gelatinised starch is known commercially as mandioc starch or as Brazilian, Bahia, Rio, or Para arrowroot.

Bitter cassava contains small proportions of hydrocyanic acid (up to 0·07%) which may be removed by pulping and washing with water. Sweet varieties may contain as much as 0·004% HCN, which is present both in the bark and edible portions of the roots.

Cassava may be boiled and eaten as a root vegetable *or dried and ground into a flour from* which bread and cakes may be prepared.

The following are typical analyses of cassava products :

	Whole root	Dried root	Peeled root	Flour	Bread	Tapioca	Mandioc starch
H_2O	63·8	10·38	61·3	5·76	26·00	9–15	12·0–16·0
Protein .	0·96	1·25	0·64	2·98	11·25	0·3–1·8	0–0·45
Fat	0·26	0·35	0·17	0·42	8·60	0·1–0·5	0·15–0·20
N-free extract .	32·7	84·36	36·5	83·8	49·11	79–89	82·9–86·9
Starch .	27·65	73·56	30·98	64·3	—	—	—
Pentosans . .	—	2·15	—	2·6	—	—	—
Fibre . . .	0·85	1·90	0·88	5·08	4·0	0·75	0·0–0·8
Ash	*0·63*	*1·76*	*0·51*	*1·96*	*1·04*	*0·2–1·0*	*0·04–0·45*
	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)		

(*a*) Adriano *et al* (Philippine Agric 1932, 20, 530).
(*b*) Kling (Landw Versuchs -Stat 1913, 82, 211)
(*c*) Ewell and Wiley (Amer Chem J 1893, 15, 285)
(*d*) Wiley (U S Dept Agric Div Chem 1894, Bull. 44).
(*e*) Gualirado (Sanidad y Benefic. 1922, 27, 145).

Wiley (*l c.*) reports the ash of peeled roots to consist of K_2O 41·6, Na_2O 1·2, CaO 10·6, MgO 7·35, Fe_2O_3 0·66, P_2O_5 15·6, SO_3 3·7, SiO_2 0·9, Cl 2·8, CO_2 9·1. A. G. Po.

CASSEL EARTH or **VANDYKE BROWN**, a highly bituminous ferruginous earth used as a pigment.

CASSEL GREEN *v* BARIUM.

CASSEL YELLOW. *Lead oxychloride.* A pigment also known as *Turner's Yellow, Montpelier Yellow, Mineral Yellow,* and *Patent Yellow.*

CASSELMANN'S GREEN is a basic copper sulphate with a bright green shade.

CASSIA. The bark of *Cinnamomum cassia* Blume (Fam. Lauraceæ), it resembles cinnamon, but is thicker, coarser, stronger and less delicate in flavour.

CASSIA, ESSENTIAL OIL OF. The oil obtained by distillation from the bark, twigs, and leaves of *Cinnamomum Cassia* Blume (Fam. Lauraceæ), cultivated in China. The residues from the cassia bark which is collected for commerce are employed for the distillation of the oil, which is carried out by natives under primitive conditions. Practically the whole of the supply is collected in South China and in French Indo China. The oil is purchased from the native distillers by dealers who sell again in local markets to larger dealers. It is then shipped to Hong Kong, which handles practically the whole of the export from China. Much of the oil is shipped in leaden canisters, but it is also available in tins and drums.

Constituents.—The main constituent is cinnamaldehyde, *of which it contains 80–90%*. Other constituents are the methyl ether of *o*-coumaraldehyde, a crystalline substance melting at 46°–47°, salicylaldehyde, coumarin, benzaldehyde, methyl cinnamaldehyde, and phenylpropyl acetate.

Characters.—The oil as imported is divided into different grades according to its cinnamaldehyde content. For many years this has been determined by adsorption with solution of sodium bisulphite, which, however, gives inaccurate results owing to the adsorption of other constituents. Efforts have recently been made to adopt the more accurate hydroxylamine method which has been adopted in the "British Pharmaceutical Codex" for the redistilled oil. By the old method the genuine oil gave an indication of 90–95% cinnamaldehyde, and this grade was reduced by the addition of a mixture of resin and petroleum to 80–85%

grade. Formerly lower grades were marketed but these have now been practically abandoned. It is hoped that the pure oil only will eventually be demanded by shippers.

The characters of the genuine oil are as follows: sp.gr. at 15° 1·055–1·070, a_D^{20} −1 to +6, n_D^{20} 1·600–1·606, it is soluble in 3 vols. of 70% alcohol. The percentage of cinnamaldehyde as determined by the hydroxylamine method is not less than 80%. This corresponds with about 90% by the bisulphite method. The oil should be free from alcohol, resin, and petroleum. Alcohol is detected by shaking with a saturated solution of brine and distilling the brine solution after shaking with light petroleum. From the specific gravity of the distillate the percentage of alcohol can be calculated. Resin is detected by adding a solution of lead acetate in 70% alcohol to a solution of the oil in 3 vols. of the same solvent. If resin is absent a clear solution is obtained. Light fractions of petroleum can be detected by distilling the oil with steam, when the petroleum separates from the distilled oil as a separate layer.

Redistilled Cassia Oil is official in the " British Pharmaceutical Codex," and in the " United States Pharmacopœia," where it is described as oil of cinnamon. The characters of this oil are : sp.gr. at 15·5 1·055–1·065, a_D^{20} +1 to −1, n_D^{20} 1·600–1·606, cinnamaldehyde content not less than 80% by weight, determined by the hydroxylamine process. Soluble in 3 vols. 70% alcohol. C. T. B.

CASSIA TORA (Linn.) or **TAGEREY-VEREY.** This plant produces grains known in the East Indies, Arabia and Japan as *Tora*, but which are known in Pondicherry and other parts of Hindustan as *Tagerey-verey*. It is regularly used as a component of the indigo vat in dyeing, apparently serving the same purpose as the bran-madder or molasses used in Europe.

The native dyers use the *Tagerey-verey* in the following manner. To dye about 200 yds. of cloth, 11¼ lb. of the grain are steeped in from 5 to 6 gallons of cold water, and then boiled for 4 hours. The grains are swollen and softened by this treatment, and the water becomes thick and gummy. The whole of this is added to the indigo vat, and after standing for 15 hours the vat is ready for use (Elborne, Pharm. J. 1889, 3, 242; Hooper, Bot. Jahresber. 1896, ii, 479).

CASSITERITE or TIN-STONE. Native tin oxide, SnO_2, containing 78·6% of tin, and practically the only ore of the metal. It varies much in appearance—the colour ranges from white to black, being usually dark brown—and its most characteristic feature is its high sp.gr. of 6·8–7·1 ; hardness, 6–7, easily scratching glass. Crystals are tetragonal, with highly characteristic knee-shaped twins ; their faces are often very brilliant with an adamantine lustre. There is an absence of cleavage ; and this readily helps to distinguish the mineral from blende. Crystals are, however, not very common, the mineral being more frequently found as disseminated grains and water-worn pebbles. Grains of cassiterite in a concentrate panned from a river sand may be readily detected by a very simple and characteristic test. When placed on a zinc plate, or in a basin with fragments of zinc, and dilute hydrochloric acid poured over, any grains of tin-stone soon show a shining white coating of metallic tin. Veins of tin ore usually occur at the junction of granitic masses and slates, and the ore also impregnates the rocks bordering the veins. Such ores are known as *vein-tin*, to distinguish them from the *stream-tin* of alluvial deposits. A compact variety with a radially fibrous and concentric structure and sometimes a botryoidal surface is known as *wood-tin*. The ore as prepared for market is known as *black-tin*, and in South America as *barilla*. The principal tin-producing countries are the Federated Malay States, the islands of Banka and Billiton in the Dutch East Indies, Siam, China, Australia (Queensland, New South Wales, Western Australia), Tasmania, Bolivia, Cornwall, and more recently South Africa (Transvaal and Swaziland) and Northern Nigeria. The production of tin ore amounts to about 170,000 tons per annum. L. J. S.

CASSIUS, PURPLE OF. A purple pigment, used chiefly in the manufacture of ruby glass, and stated by Haber (Physikal. Z. 1924, 25, 45) to be a mixture of colloidal gold and colloidal stannic acid. It can be made by adding tin chloride to a solution of ferric chloride until a green colour is produced. The solution is then added gradually to a solution of gold chloride ($AuCl_3$). It was discovered before 1685 by Andreas Cassius.

CASTELAGENIN *v.* CASTELIN.

CASTELIN, $C_{15}H_{22}O_8 3Aq$. M.p. 205°. $[a]_D$ +62·9°, is a glucoside isolated and named by Bosman (J.C.S. 1922, 121, 969) from the bitter bush (*Castela Nicholsoni*) and other Simarubaceæ, decoctions of which have for centuries past been used for dysentery, malaria, etc., by the natives of China, Mexico and Texas. It is hydrolysed by 20% hydrochloric acid to glucose, and an aglucone, *castelagenin*, of unknown constitution. E. F. A.

CASTOR or CASTOREUM. This substance is one of the few animal perfume materials, analogous to civet and musk. It is a secretion of the beaver (*castor fiber*) contained in cellular glands situated under the abdomen, near the genital organs. These glands are cut out and dried. The secretion, which is soft at first but hardens on keeping, is occasionally used in medicine, its main use being in perfumery. It is collected by native Canadian hunters and brought in to the Hudson Bay Company's depot, who may be said to hold the monopoly of the product.

Little is known of its composition. In 1848 Wöhler (Annalen, 1848, 67, 360) made a cursory examination of it and stated that phenol was present. It has been found to yield 2·1% of essential oil, which contains *o*-cresol, a phenol $C_{12}H_{16}O_2$, acetophenone, benzyl alcohol, *l*-borneol, *p*-ethylphenol, and a methoxy-containing phenol (Walbaum and Rosenthal) (J. pr. Chem. 1927, [ii], 117, 225). These chemists consider that the phenolic bodies are in part, at least, due to the smoke of the fuel used in drying the organs of the trapped beavers. St. Pfau (Perf. & Essent. Oil Rec. 1927, 18, 206)

has also found present a characteristically odorous lactone, and also ethylphenol.

A genuine castor should yield between 85 and 90% when extracted with ether. The ash should not exceed 1%. E. J. P.

CASTOR OIL is obtained from the seeds of *Ricinus communis*, L., and *R. sanguineus* (the red or purple castor). The former plant appears to be indigenous to Africa (Egypt), but was transplanted to India at a very early stage of history, so that some writers consider the plant indigenous to India itself. The plant grows in enormous quantities in all tropical and subtropical countries, and is even found wild to day in South America, notably in Paraguay and the Argentine. The purple castor is best acclimatised in North Africa and the Mediterranean area (Morocco, Italy, Egypt, etc.), and is especially valued for the production of pharmaceutical oils.

Numerous closely allied species of *Ricinus* are known, but have not yet been exploited on any large scale, although in some cases the seeds contain considerably greater amounts of oil than the commercial varieties (*e.g.* 60–70%, and even 85%), for an account of these plants and their oils, *see* Bessé (Thesis, Paris, 1929), André and Bessé (*Bull. Sci. Pharm.* 1931, 38, 487), Eberhardt ("Le Ricin," Paris, 1931), Shrader (U.S. Dept. Agric. Bull. 867, 1920).

The most important sources of castor seed are East India (which furnishes about three quarters of the world's crop), Java, the Mediterranean countries, Mexico, and the United States of America, whilst the cultivation of the plant has of recent years been developed in the Egyptian Sudan, Fiji, the East African Protectorates and South Russia.

The seeds consist of 20% of husks, which are rich in mineral matter, but contain no oil, and 80% of kernels, forming a white, softish mass. The seeds contain the toxalbumin *ricin*, or *ricinine* (*cf.* Osborne, Mendel and Harris, Z. anal. Chem. 1907, 46, 213; S. Inowe, J. Soc. Chem. Ind. Japan, 1937, 40, 122B).

The kernels contain a powerful fat-hydrolysing enzyme (*lipase*); advantage is taken of the presence of this natural fat splitting agent in the commercial process for the production of fatty acids from oils (particularly from castor oil) by the "enzyme" or "ferment" process of *saponification*, in which a "ferment" prepared from macerated castor seed is employed to catalyse the hydrolysis of the oil. The lipase can be extracted from castor beans by means of ether (Falk and Sugiura, J. Amer. Chem. Soc. 1915, 37, 217). Castor lipase is able to catalyse the hydrolysis of oils at temperatures as low as −5°C. (Blanchet, Compt. rend. 1914, 158, 895), Willstätter and Waldschmidt-Leitz (Z. physiol. Chem. 1924, 134, 161), in agreement with Haley and Lyman (J. Amer. Chem. Soc. 1921, 43, 2664) and Falk (*ibid.* 1926, 48, 1655) have shown that the lipase ("spermatolipase") present in ordinary resting (dormant) castor-seed possesses lipolytic activity in acid media at an optimum p_H of 4·7–5 (*cf.* Tanaka, J. Coll. Eng. Tokyo, 1912, (v), No. 4, 125; J. Soc. Chem. Ind. Japan, 1918, 21, 112; Armstrong and Gosney, Proc. Roy. Soc. 1913, B, 86, 586; 1915, B, 88, 176). When castor seed germinates, the lipolytic enzyme changes its character, and is converted into the enzyme "blastolipase" (Willstätter and Waldschmidt-Leitz, *l.c.*) which displays maximum activity in neutral solution (*cf.* Padoa and Spada, Giorn. biol. appl. ind. chim. 1931, 1, 81; Connstein, Hoyer, and Wartenberg, Ber. 1902, 35, 3988); this change appears to be the result of the action of a proteolytic seed enzyme on the protein like colloidal carrier of the castor lipase (*cf.* Waldschmidt-Leitz, Chem. and Ind. 1936, 625). (For the preparation of technical castor seed ferment, *see* Kita and Osumi, J. Soc. Chem. Ind. Japan, 1923, 26, 11B; Sudborough, J. Indian Inst. Sci. 1922, 5, 119.)

The hydrolysis reaction is a reversible one, and, under suitable conditions, lipase is capable of inducing the synthesis of mono-, di-, and tri-olein from an emulsion of oleic acid and glycerol (Krausz, Z. angew. Chem. 1911, 24, 829).

Castor seeds contain about 46–55% of oil, on the manufacturing scale, about 40% (on the seed) can be recovered by expression. For the production of the best quality oil (for medicinal purposes and for aero engine lubrication), the seeds are decorticated before being expressed in the cold. The press cake is subjected to a second and third expression, but the oils so obtained are unfit for medicinal use, and are employed for technical purposes (soap making, Turkey-red oils, and lubricating oils). The lowest grade of oil is obtained by solvent extraction (usually with carbon disulphide) from the final press residues.

The cakes retain the toxalbumin, *ricin*, and are therefore unfit for feeding purposes. Although various methods for removing the ricin have been proposed (*cf.* Indian Trade J. 1908, 9, 309; 1909, 11, 273; Petrosyan and Ponomarev, Schweinezucht, 1934, 4, 33), castor cake has not yet been used as cattle food; it is largely employed, however, as a fertiliser, being rich in nitrogen (*cf.* Bull. Imp. Inst. 1911, 9, 33).

A simple physiological method of detecting *castor seed in other seeds* is described by Lander and Geake (Analyst, 1914, 39, 292); for a review of other suggested methods, *see* Wagenaar (Z. Unters. Lebensm. 1929, 57, 413), and Better (Allgem. Oel- Fett Ztg. 1932, 29, 541).

Castor oil is a colourless or pale greenish oil, having a taste at first mild, then harsh, but the finest medicinal quality is practically tasteless, the harsh taste is more pronounced in American than in Italian or French oils. Castor oil is non-drying, and has the following analytical characters: sp. gr.$_{15.5}^{15.5}$ 0·959–0·968, refractive index 1·477–1·479/20°C., iodine value 81–90, saponification value 175–183, acetyl value 133–154 (usually about 150), unsaponifiable matter 0·4–0·7%, melting-point of fatty acids 13°C. (Bessé, Thesis, Paris, 1929; *cf.* André and Bessé, Bull. Sci. Pharm. 1931, 38, 487, reports sp. gr.$_{15}^{15}$ 0·9485–0·9532, saponification values 178–192, and acetyl values of 106·5–134·2 for castor oils extracted by means of carbon disulphide). The setting point of expressed castor oil, viz. −10° to −18°C. is exceptionally low.

The oil is strongly dextro-rotatory ($[\alpha]_D$ +7·6 to +9·7, Deering and Redwood, J.S.C.I. 1894, 13, 959 ; *cf.* Bessé, *l.c.*)., the optical activity being due, probably, to the presence of an asymmetric carbon atom in the constituent ricinoleic acid (*cf.* André and Bessé, Ann. combust. liq. 1931, 6, 245).

Castor oil is characterised by the presence in predominating amount of glycerides of ricinoleic (11-hydroxystearic) acid, as a consequence of which the oil is distinguished from all other commercial fatty oils not only by its optical rotation but also by its high specific gravity and acetyl value (*see above*), and by its complete miscibility with absolute alcohol and glacial acetic acid, and its insolubility in large quantities of light petroleum, kerosene or high-boiling paraffin oils.

The oil gives a homogeneous solution with an *equal* measure of light petroleum, or with 1½ vols. of kerosene ; if more solvent is used, the excess will float on the top of the mixture. If castor oil be mixed with a small quantity of another fatty oil, the characteristic insolubility in petroleum distillates is lost.

Castor oil also possesses the highest viscosity of all known fatty oils, only " blown " oils and rosin oil approaching it in this respect ; typical values are shown in Table I below, in which some figures for competing solvent-treated mineral oil lubricants have been included for comparison :

TABLE I.—VISCOSITY OF CASTOR OIL, ETC.

	Castor oil.		Solvent-treated mineral oil.	
	First pressings.	Second pressings.	" Aviation."	"Heavy Aviation."
Viscosity, Redwood—	Secs.	Secs.	Secs.	Secs.
At 70°F. . .	4,250	3,600	3,200	4,400
At 100°F. . .	1,160–1,190	—	1,000	1,350
At 140°F. . .	340–350	335	1,320	410
At 200°F. . .	95	95	100	120
Viscosity index .	80	87	102	108
Open flash point.	542°F.	500°F.	—	—
Sp. gr. at 60°F. .	0·960–0·968	0·962	0·882	0·888

The fatty acids of castor oil consist of 80–82% of ricinoleic acid, 7–9% of oleic, 1–3% of linolic, and 2–5% of stearic and dihydroxystearic acids (*cf.* Eibner and Münzing, Chem. Umschau, 1925, 32, 153 ; Heiduschka and Kirsten, Pharm. Zentr. 1930, 71, 81 ; Panjutin and Rapoport, Chem. Umschau, 1930, 37, 130 ; Toyama and Ishikawa, Bull. Chem. Soc. Japan, 1936, 11, 735 ; Bömer and Brehm, Z. Unters. Lebensm. 1936, 72, 1). The bulk of the ricinoleic acid is present as the glyceride *tri-ricinolein* ; in addition, *di-ricinoleo-stearin* and *di-oleo-ricinolein* have been identified by Eibner and Münzing (*l.c.*), whilst André (Compt. rend. Congrès du Graissage, Strasbourg, 1931) records the presence of *di-ricinoleo-linolin* and *di-ricinoleo-mono-dihydroxystearin*.

Crude castor oil intended for lubrication may be refined by steaming the oil, in order to inactivate any lipase present and to coagulate albuminous impurities, so that they can be removed by filtering ; the oil is then deacidified with caustic soda if necessary. According to Russian experience, however, it is preferable that the oil should not be filtered before the treatment with alkali, as the presence of the albuminous matter is stated to facilitate the separation of a coarse-grained soap-stock (*cf.* R. Heublyum, Allgem. Oel- Fett-Ztg. 1933, 30, 77).

The medicinal use of castor oil is well known ; the cause of the purgative action is not yet fully understood, but it appears to be associated with the oil itself (ricinoleic glycerides) and not with any adventitious constituent (*cf.* Normann, Z. Deuts. Oel- u. Fett-Ind. 1926, 46, 193 ; Heiduschka and Kirsten, *l.c.* ; Valette and Salvanet, Compt. rend. Soc. Biol. 1936, 122, 68).

Owing to its extremely low setting-point, high viscosity, and its comparatively flat temperature-viscosity curve (viscosity index 80–90), castor oil has proved a very valuable lubricant for internal combustion engines, and in particular for racing motor-cycle and aeroplane engines. For the latter purpose the highest quality of cold-pressed oils is employed. The specification for castor oil for lubrication drawn up by the Air Ministry of Great Britain (Air. Min. Spec. DTD 71) requires that the oil shall have : sp.gr.$^{60°F.}$ 0·959–0·968, viscosity at 200°F. not less than 20 centipoises (about 93 seconds, Redwood), acid value not over 3·5, unsaponifiable matter not exceeding 0·8%, iodine value 82–89; in addition the oil must remain perfectly clear when exposed (in a closed tube) to a temperature of −10°C. for 4 days, and a solution of 1 part of oil in 4·15 parts (by weight) of alcohol (sp.gr.$^{15·5}$ 0·8303) must be perfectly clear at 20°C., and must remain clear when cooled to 0°C. for 5 minutes. The requirements of Air Min. Spec. DTD 72 for " treated " castor oil (presumably demargarinated oil) are more stringent as regards the cold test (10 days at −10°C. without turbidity) and the alcohol-solubility test (*cf. also* British Standard Specification 650/1936 for castor oil (" firsts ") quality, and Specification of U.S. War Dept. (Castor oil for internal combustion engines is, however, now being displaced to some extent by special grades of heavy mineral lubricating oils which have become available since the introduction of the newer solvent-processes of refining, *cf.* Table I.) Stable compound oils consisting of castor oil with 5% of mineral oil, or mineral oil containing 5% of castor oil, are also used as lubricants.

An important class of materials of the type of " Turkey-red Oils " is obtained by the more or less intensive sulphonation of castor oil; these products, which originally acquired importance as mordants in alizarin dyeing, are extensively used as wetting-out and emulsifying

agents in the dyeing and finishing of textiles, in the preparation of "soluble" (i.e. emulsified) lubricating oils (cutting oils, etc) and in the leather industry for the fat liquoring of leather

Castor oil itself is also employed in the manufacture of transparent soaps, as a softener for nitrocellulose lacquers, e.g. for artificial leather finishes and aeroplane "dopes" (cf British Standard Specification 3D5 Aircraft Materials—"Castor oil for nitro dope coverings") and, more recently, as an ingredient of synthetic resins and plastics. The oil also finds minor applications as a dressing for leather-belting, in the preparation of fly gums and other adhesives, and in pharmacy as a hair oil and massage oil

On subjecting castor oil to destructive distillation, "cognac oil," a mixture of undecylenic acid and heptaldehyde (oenanthaldehyde) is obtained, whilst pyrolysis of the sodium soaps of castor oil fatty acids yields sec octyl alcohol and methyl hexyl ketone, all these materials are important intermediates in the perfume industry, heptaldehyde forms the basis for the preparation of the synthetic "jasmine" perfumes.

The use of castor oil (ricinoleic acid) as a raw material for the preparation of an artificial drying oil has been patented by Scheiber, U S.P. 1942778

By heating castor oil for 10 hours at a temperature of 260°–300° under a pressure of 4–6 atms., it becomes miscible with mineral oils (cf H. Nordlinger, G P. 104499, Villiers London Co, B P 193099, Reizenstein, U S.P. 1715785) Such products (marketed in Germany under the name *Floricinoel* or *Dericinoel*) found some use at one time as ingredients of compound lubricating oils, but appear to have fallen into disuse When heated at 150°–250°, and then neutralised with alkali, castor oil yields soaps which are soluble in hydrocarbons

The figures below illustrate the extent of the castor oil industry. (N.B.—Figures in tons: average oil content of seed 42%) (Selected from Rev. of Oilseed, etc, Markets for 1937, Frank Fehr & Co).

TABLE II.

	1934	1935	1936	1937.
Seed.				
Indian production	116,000	109,000	122,000	126,000
U.K imports	35,415	36,308	29,937	32,412
French imports	18,800	20,900	21,571	17,951
U.S imports	41,447	34,400	73,245	65,147
Japanese imports	17,563	18,570	27,620	not available
Oil.				
European countries production	30,000	40,000	35,000	35,000
U S A. production	17,407	14,448	30,762	27,361

Figures indicating the present production of castor seed in South Russia are not available, but it is stated to be sufficient to provide for internal needs and a balance for export.

J. L. and E. L.

CATALASE. The word is a collective term for those enzymes which destroy hydrogen peroxide. Catalases of different origin may be supposed to differ according to the nature of their colloidal carriers.

Active preparations can be made from most cells, the purest and most stable are made from liver extract (Zeile and Hellström, Z. physiol. Chem. 1930, **192**, 171; 1931, **195**, 31). Vegetable catalase is much less stable. Catalase activity has been correlated by Zeile with the hæmatin iron content attached to a colloid component. Haldane (Proc. Roy. Soc. 1931, B, **108**, 559) calculates that an atom of catalase iron will at 0° decompose from 6×10^4 to 2×10^5 molecules of H_2O_2. These figures are of the same order as those for the iron in peroxydase and in the respiratory ferment. (For a recent account, *see* Zeile, Ergebnisse der Enzymforschung, 1934, **3**, 265)

According to Stern (Nature, 1935, **136**, 302, 335) the hæmatin group has a porphyrin skeleton with the same arrangement of the side-chains as in the natural blood pigment. The colloid is considered to be a protein. Agner (Z. physiol Chem. 1935, **235**, 11) claims indeed to have separated catalase by dialysis against acid solution into two fractions, the prosthetic group and the protein, each alone being inactive but regaining activity on mixing. E. F. A

CATALIN (trade name). Cast phenol formaldehyde condensation products manufactured by the Catalin Corporation in the form of rods, tubes, sheets and special castings

E. E W.

CATALPO. Trade name for a colloidal china clay, used in paint and rubber manufacture.

CATALYSIS IN INDUSTRIAL CHEMISTRY. The applications of catalysis in industrial chemical processes have undergone remarkable developments during the present century, especially in the field of heterogeneous catalysis, i.e. actions which take place between gases and/or liquids at a specific solid surface of suitable physical form. There are also, however, many important instances of homogeneous catalytic actions which are used in industry. The theoretical background of catalytic actions, especially those at the surfaces of solids, has been to a certain extent made clear as the result of multitudinous investigations undertaken in laboratories in many parts of the world. At the present time we possess at least a working picture of the mechanism by which a solid catalyst acts, and of the important part played by selective adsorption of the various interactants by the solid catalyst; we differentiate between general or "physical" adsorption and the "activated adsorption" or "chemisorption" which is the precedent to actual catalytic interaction In a catalyst especially we have realised that, as first emphasised by H. S Taylor, we are not concerned with the average behaviour of atoms or molecules in the mass, but with the properties of a select few of the individual atoms or molecules present. Recent research has in part been directed to attempts to define which particles in a solid surface (e g. possibly those lying along

phase or micro-crystal boundaries) possess the essential properties of a catalyst—and why; but here we are still very much in the region of uncertainty, or even speculation. The theoretical or "fundamental" investigations which are of immediate value to the technician are those (*e.g.* studies of adsorption and thermal effects, etc.) which have indicated the conditions essential to an active catalyst surface and those which tend towards increased activity on the one hand (catalyst activators or stimulants), and retarded activity on the other (catalyst "poisons," "negative catalysts"). Further, physical chemistry plays an important part in the use of catalytic processes, and their utilisation is frequently helped by considering specific problems in the light, for example, of the Le Chatelier Principle or of Nernst's Heat Theorem, to mention two of many instances.

No attempt can be made in this article to give a complete account of industrial catalytic processes, the details of which will be sought in articles dealing with each individual product. *The present purpose is to survey the whole* field of technical catalytic processes so as to focus attention, in the first place, upon the more important products manufactured by catalytic agency, and, in the second place, upon the nature and functions of the many substances used as catalysts and upon the different physical conditions under which different catalytic processes proceed to the best advantage. The variety of elements and compounds which exhibit useful catalytic properties, in one direction or another, is enormous; but while non-metallic elements, salts, and more complex compounds are all to be found amongst catalysts employed at the present time, it is true to say that the active agent is most frequently a specific metal or metallic oxide, or, often, a binary or ternary mixture of metals or of their oxides. The temperatures and pressures at which catalytic processes are carried on vary widely. Some actions, such as the condensation of acetaldehyde to ethyl acetate or crotonaldehyde (aldol), require a very low temperature; many others take place over the range 100°–250° and not a few at 400°–500° or even higher. Similarly, working pressures range from atmospheric through moderately high (10–20 atms.) to very high pressures (250–1,000 atms.), the latter having been developed for the most part within the last quarter of a century. Some of the more important materials produced technically by catalytic action will now be considered, commencing with inorganic substances and proceeding subsequently to the chief applications of catalysis in the manufacture of organic compounds, including a reference to those cases in which enzymic catalyses (fermentation) are conducted on an industrial scale.

SULPHURIC ACID.—(i) *Chamber Process.*—The old chamber sulphuric acid process was one of the rare cases of a homogeneous catalytic process taking place in the gaseous phase—although probably part of the oxidation of sulphur dioxide to trioxide always occurred, even in the older plants, in the liquid phase (in aqueous solution either as mist or on the walls of the chambers). In modern practice the aim has been to reduce the chamber space by injecting water sprays instead of steam (Meyer, Mills-Packard) or by operating in a plant constructed similarly to a fractionating column, down the trays of which acid or water flows in counter-current to the ascending burner-gases (Opl). The use of these or similar devices has led to considerable reduction in the cubic space of plant necessary to produce a given output of chamber acid, and has enabled the chamber process to continue to compete effectively with the contact process so far as the manufacture of ordinary concentrated (96%) sulphuric acid is concerned.

(ii) *Contact Process.*—The oxidation of sulphur dioxide by oxygen at a platinum surface, originally patented by Phillips in 1831, was first conducted successfully on a commercial scale by Squire and Messel in 1875; but the sulphur dioxide had to be produced from sulphuric acid or specially purified sulphur, because the platinum rapidly lost its activity when pyrites gases were used. After Knietsch had shown (about 1900) that arsenic and other impurities in the sulphur dioxide were the cause of the "poisoning" of the platinum catalyst, means were devised for suitable purification of the pyrites gases and several forms of contact sulphuric acid plant were thereafter designed. In the Badische process asbestos fibres impregnated with platinum are employed in a series of vertical iron tubes at 400°–450°, down which the pre-heated mixture of purified sulphur dioxide and air is passed. In the Grillo process the catalyst is platinum deposited on hydrated magnesium sulphate, which (after calcining) is set on a number of superimposed horizontal trays in a vertical converter; this is a very compact and efficient plant and it is claimed that a ton of oleum can be produced daily from about 1·75 kg. of catalyst containing only about 5 g. of platinum. In the Mannheim process, the crude gases from the pyrites burners are first passed through beds of burnt pyrites (iron oxide) at 600°–700°, which serves not only to remove arsenical, etc., impurities, but also to effect conversion of about half the sulphur dioxide to trioxide; the latter is removed by scrubbing through concentrated sulphuric acid and the residual, purified gases are passed through a platinum catalyst converter to effect the oxidation of the rest of the sulphur dioxide. About 1928 the use of vanadium pentoxide (which had been found an efficient catalyst for the controlled oxidation of naphthalene and other hydrocarbons by means of air, *cf. below*) in place of platinum was proposed, and at the present time a number of contact sulphuric acid plants of this kind are being successfully operated. The vanadium oxide is frequently prepared in the form of an artificial zeolite (in which it has replaced the soda of the original zeolite). The process is worked at 450°–500° and it is claimed that, whilst giving a conversion equal to that obtained with platinum, vanadium oxide is not only cheaper than the latter but is also less sensitive to the toxic action of impurities.

AMMONIA.—Haber and his students showed that the nitrogen-hydrogen equilibrium data

indicate that direct union of these gases (to ammonia) is feasible at 400°–500° and pressures of 100 atms. upwards, providing that attainment of the equilibrium can be suitably accelerated; they also found a number of metallic catalysts which bring about rapid establishment of the equilibrium. The process was studied intensively by the Badische Co. with the aim of large scale synthesis of ammonia and in 1913 the first plant came into operation at Oppau with an output of 130,000 tons of fixed nitrogen per annum. The German plants operate the Haber-Bosch process in which nitrogen and hydrogen in the correct proportions (made catalytically from water gas and producer-gas with steam, *cf.* Hydrogen below) are circulated over reduced iron oxide (containing a small proportion of caustic soda or potash) at 550°–600° and 200 atms pressure. About 8% of the gases are converted to ammonia at each passage over the catalyst. During and since the war of 1914–1918 the production of synthetic ammonia has been undertaken on a very large scale in many countries. In England the factory of Imperial Chemical Industries at Billingham-on-Tees is the centre of production; a modified form of the Haber-Bosch process is employed, the working pressure being 250–300 atms

Most of the plants in other countries also operate at 200–300 atms, and the chief differences are connected with the production of the nitrogen hydrogen mixture according to local conditions. Where electricity is very cheap, *e g.* in Italy, the hydrogen is obtained by electrolysis of water, and it becomes necessary to prepare separately the corresponding quantity of nitrogen; in different processes this is effected by (i) fractionation of liquid air, (ii) utilisation of residual nitrogen from air used in the oxidation of some of the synthetic ammonia to nitric acid (Fauser), or even (iii) burning a mixture of electrolytic hydrogen and air in the steam raising plant (Casale). In the majority of cases where coal forms the ultimate source of hydrogen, water gas and producer gas are mixed and treated with steam by the catalytic process wherein carbon monoxide and steam *yield hydrogen and carbon dioxide, the* proportions of the two gases being so adjusted that the final product (after removal of carbon dioxide by solution in water at about 30 atms pressure and of carbon monoxide by ammoniacal cuprous solutions at 200–250 atms. pressure), contains slightly more than 3 vols of hydrogen to 1 of nitrogen. The use of pressures as high as 1,000 atms. has been advocated (Claude) in order to effect much higher conversion of the nitrogen-hydrogen mixture at each passage over the catalyst and to secure a more compact plant.

The production of sulphate of ammonia is now usually effected by double decomposition of ammonium carbonate (from the carbon dioxide produced in the manufacture of hydrogen) and natural calcium sulphate (anhydrite), instead of by direct neutralisation of ammonia liquor with sulphuric acid (*see* AMMONIA).

NITRIC ACID.—This is now manufactured almost exclusively by the catalytic oxidation of ammonia with air, the nitric oxide first formed ($4NH_3+5O_2=4NO+6H_2O+211.2$ kg.-cal.) being converted by excess oxygen into nitric peroxide, which in presence of water yields nitric acid and nitric oxide. The oxidation is effected by passing 1 vol. of ammonia mixed with about 8 vols. of air over a small layer of platinum gauze at 700°–800°; the gases must be carefully filtered from metal oxide dust before contact with the platinum, and the time of contact must be rigidly controlled (0.001 second) to avoid decomposition of the nitric oxide into nitrogen and oxygen. The process (first suggested by Kuhlmann in 1839) was not successfully worked on a large scale until just before the war of 1914–1918. On a technical scale the efficiency of the oxidation is nowadays over 93% and the overall efficiency (*i.e.* including the further conversion of nitric oxide to nitric acid) nearly 90% of the theoretical Certain mixed oxides, especially iron oxide mixed with about 3% of bismuth oxide, are also effective oxidation catalysts for ammonia, and have been used to a certain extent in large scale production; but the platinum gauze process appears at present to hold the field.

The catalyst chamber is the smallest unit in an ammonia–nitric acid plant, owing to the exceedingly rapid and complete production of nitric oxide, the conversion of which into nitric acid requires much more space. The gases from the catalyst converters are cooled, mixed with more air, and passed through scrubbing towers in counter-current with water. The oxidation of nitric oxide to peroxide is relatively *slow, compared with that of ammonia to nitric* oxide; moreover, one-third of the nitrogen peroxide is re converted into nitric oxide (which must again be oxidised) when the former reacts with water ($3NO_2+H_2O=2HNO_3+NO$). The process is usually controlled so that a 50% solution of nitric acid is finally obtained, whilst the final portions of the nitrogen peroxide (about 5–10% of the whole) are absorbed by soda to form sodium nitrate. The main nitric acid solution is concentrated by vaporising through "denitrating" towers down which a constant stream of concentrated sulphuric acid is passed

REMOVAL OF SULPHUR COMPOUNDS FROM GASES.—The removal of hydrogen sulphide or gaseous compounds of sulphur and carbon (carbon disulphide or oxysulphide, alkyl thiols or sulphides) from commercial gases such as coal-gas or hydrogen is largely effected by catalytic agents (metals or metallic oxides). When coal-gas is mixed with a very small proportion of air and passed through iron oxide purifiers *hydrogen sulphide* is converted into sulphur,

$$2H_2S+O_2=2S+2H_2O,$$

and the process can be pursued until the iron oxide is sufficiently rich in sulphur to be worked up by the sulphuric acid manufacturer; by this means the older alternate use of iron oxide for the removal of hydrogen sulphide, followed by aeration, becomes a catalytic process. The use of the Claus kiln in the Chance method of recovery of sulphur from alkali waste is another technical application of the same catalytic action. *Organic sulphur compounds* present in

technical gases are completely converted into hydrogen sulphide and carbon compounds when passed over heated iron oxide or iron at 500°, especially if steam be present (*e.g.* in the manufacture of hydrogen from water-gas, etc., *cf. below*), or even at lower temperatures (Guillet); they are also broken down into hydrogen sulphide by passage over nickel on fireclay at 450° (South Metropolitan Gas Co.) or over iron chequer work (as in a water-gas plant) at 700°–900°.

HYDROGEN.—In addition to the manufacture of hydrogen by electrolysis of water, or by the alternate passage of water-gas and steam over iron oxide ores heated at about 700°–800°, two important catalytic methods have been developed to meet the growing demand for pure hydrogen. One of these depends on the equilibrium $CO+H_2O \rightleftharpoons CO_2+H_2+10$ kg.-cal., the other on the equilibrium

$$CH_4+H_2O \rightleftharpoons CO+3H_2-48{\cdot}9 \text{ kg.-cal.}$$

(i) *The Water-gas–Steam Reaction.*—Water-gas, or a mixture of water- and producer-gas, is mixed with an excess of steam and passed through converters containing (reduced) iron oxide at 450°–500°. With efficient heat-interchange between the exit and inlet gases, the heat of reaction suffices to maintain the catalyst at the required temperature, once the reaction has been initiated. The emerging gases contain about 2% of carbon monoxide which, after removal of the carbon dioxide formed (by washing with water after compression to 50 atms.), is absorbed by scrubbing at higher pressures through ammoniacal copper formate solution. Hydrogen is largely manufactured by this process for high-pressure hydrogenations such as the synthesis of ammonia or methanol and the hydrogenation of heavy oils or coal into petrol.

(ii) *The Methane–Steam Reaction.*—This is catalysed most effectively by nickel; at low temperatures (300°) the equilibrium is largely in the direction of formation of methane, but at 800°–900° it is in the opposite sense, and methane and steam can be converted into carbon monoxide and hydrogen. This has recently been utilised in the commercial production of hydrogen from waste gases rich in methane and ethane (which undergoes a similar change), such as natural gas from petroleum deposits, and the permanent gases produced during cracking of petroleum or during the conversion of coal into liquid hydrocarbons. A preheated mixture of such gases and steam is passed over a nickel-corundite catalyst at 860°–900°, when it is converted into carbon monoxide and hydrogen; the gases so produced are cooled to about 500°, and then submitted to the "water-gas–steam reaction" in presence of iron. In this way a gas originally containing about 80% methane and 17% ethane is transformed into a mixture of about 78% hydrogen, 20% carbon dioxide, and 2% of methane and carbon monoxide, from which the carbon dioxide and monoxide are separated as already described. This process is coming into use as a main source of the hydrogen required for high-pressure hydrogenation-cracking of coal, tar oils, or heavy petroleum residues into low-boiling hydrocarbons.

ALCOHOLS AND HYDROCARBONS FROM CARBON MONOXIDE.—In addition to its catalytic (iron oxide) conversion, with steam, into *hydrogen*, it should be noted that water-gas, alone or mixed with steam, is transformed into *methane* and carbon dioxide by passage over nickel at suitable temperatures. Next to hydrogen, however, the most important product obtained from water-gas is *methyl alcohol*, which results when the mixture of carbon monoxide and hydrogen is passed at 100–200 atms. pressure and about 400° over a mixture of zinc and chromium oxides (basic zinc chromite). This is now by far the most important source of supply of methyl alcohol, the total world-production of which from water-gas in 1935 was about 75,000 tons. If, instead of zinc-chromium oxides, an alkalised iron catalyst is employed, the liquid product, "synthol," obtained is a mixture of alcohols, ketones and hydrocarbons containing from 2 to about 8 carbon atoms per molecule.

Passage of carbon monoxide and methyl alcohol over phosphoric acid at about 350° and 200 atms. pressure leads to the production of *acetic acid* in technical yields. It seems that this process may develop into an active competitor with the present catalytic methods (*v.* acetic acid) whereby acetic acid is manufactured almost entirely from acetaldehyde, which in turn is produced from alcohol or acetylene.

An important process for catalytic conversion of water-gas into motor fuels is that of Fischer and Tropsch, namely, passage of carefully purified water-gas over certain mixed catalysts (for example, iron oxide or cobalt oxide with small amounts of thoria, deposited on kieselguhr) at 180°–200° and atmospheric pressure. By this means, with careful precautions in gas-purification and in exact control of temperature, about 80% of the carbon monoxide is obtained in the form of a mixture of hydrocarbons. Of these, the lower-boiling fractions make excellent Diesel engine fuel or, blended with benzols or other anti-knock fuels, petrol for the ordinary internal-combustion engine; while from the higher fractions, which are olefinic in character, lubricating oils of high quality can be produced by chlorination and subsequent Friedel-Crafts condensation with the original oil or with aromatic hydrocarbons. This process is making great headway in Germany, where plants with an annual capacity of about 170,000 tons of motor spirit from water-gas are coming into operation (1936). A very important asset in the Fischer-Tropsch process is the practicability of converting the higher hydrocarbon products into good lubricating oils. In contrast to the "hydrogenation-cracking" or degradation processes of complex cyclic hydrocarbons about to be described, the production of hydrocarbon fuels from water-gas involves the building-up of aliphatic hydrocarbon chains, the higher members of which can then be further condensed into long-chain compounds with good lubricant properties.

HYDROGENATION-CRACKING OF COAL, TAR OILS, HEAVY PETROLEUM RESIDUES.—Processes are now in operation on a technical scale whereby powdered *coal* is converted, at high temperatures

and pressures, and in presence of solid catalysts, into liquid hydrocarbon products. By conducting the pressure-hydrogenation in two stages, the coal has been transformed into a *light oil (petrol)*, suitable for the ordinary internal combustion engine, in yields sufficiently high (165 gallons of petrol per ton of coal used in the process and for heat, power, etc) for the cost of the product to bear comparison with that of motor spirit from petroleum. In the first (liquid phase) stage, a suspension of finely powdered coal is made into a paste with "heavy oil" already produced in the process, mixed with a *small proportion of a catalytic material (certain* compounds of tin are stated to be most active) and injected with hydrogen at 250 atm. pressure through converters maintained at about 400°. The solid coal is thereby converted into a mixture consisting mainly of heavy oil with a certain proportion of light oil and permanent gas, which is separated by distillation into the light and heavy oils and a comparatively small non volatile residue In the second stage, the heavy oil is subjected to a "hydrogenation cracking" process in the vapour phase by passage, with hydrogen, at about 200–250 atm and 450° over a pelleted catalyst composed of molybdic acid to which sulphur has been added; here the heavy oil is more or less completely converted into *light hydrocarbon spirit* with a certain amount of gaseous products (chiefly methane). The products from the second stage are separated by distillation, and residual heavy oil re cycled. The gaseous products from both stages are collected to serve as material for further production of hydrogen as described above.

The high pressure "hydrogenation cracking" in presence of molybdenum oxide catalyst is also applied directly in the production of motor spirit from the higher boiling *coal-tar* or *creosote oils*, produced either in the high or low temperature carbonisation of coal, and from the residues from the distillation of crude or cracked crude petroleum. Hydrogenation cracking is a very important instance of modern industrial catalytic processes, since it has provided additional *sources of motor* spirit and has also afforded a means of profitable use of the awkward by-products from the distillation of coal tars and of crude petroleum, as well as affording a new outlet for coal itself. The process is also applied to the hydrogenation and desulphurisation of lubricating oils and naphthas, the refining of burning oils, and the conversion of gas oils into anti knock petrol.

HYDROGENATION.—Many of the technical catalytic methods referred to in the preceding paragraphs concern hydrogenation processes (*e.g.* the production of ammonia, methyl alcohol, motor spirit), but there remain a number of cases of straightforward addition of hydrogen to unsaturated organic compounds, or reduction of oxygenated organic compounds, to which reference should be made. These, and indirectly all the more recent technical applications of catalytic hydrogenation and dehydrogenation, are ultimately largely the result of the pioneer work of Sabatier, Senderens and, Mailhe in the years 1897–1910 on the action, especially, of nickel, copper and cobalt as catalysts for hydrogenation or dehydrogenation of organic compounds in the vapour state Thus, for instance, hydrogen has been found available for many operations of reduction and of hydrogenation when used along with various catalysts. In the former class of reactions nickel is in general very effective, but as it is sensitive to "poisons," particularly sulphur compounds and carbon monoxide, care must be taken that both the hydrogen and the substance to be attacked are freed from such impurities Palladium and platinum, especially when in *the colloidal state, are also active* catalysts of such reactions. The operations may be carried out either at the ordinary or at increased pressure, and either at such temperatures that the reacting substances are vaporised or at the ordinary temperature with the substances in the liquid state or in solution. With nickel as catalyst the addition of hydrogen to unsaturated compounds, when in the state of vapour, is easily effected. Ethylene, for example, is readily converted into ethane at 140°–170°, and the preparation of hexahydro-derivatives of benzene and other aromatic compounds is carried out with little difficulty. A most useful application of the process of hydrogenation was initiated when Normann demonstrated in 1902 that Sabatier's methods could equally well be applied to organic compounds in the liquid state, and showed that liquid fats (fatty oils) could be converted into solid fats melting over the range 25° to about 70° (the latter being the melting point of a completely saturated fat). This "fat hardening" process depends essentially upon the conversion of polyethenoid glycerides into oleo-glycerides and, finally, into stearo glycerides It came into technical operation about 1910, and forms by far the largest application of catalytic hydrogenation of organic compounds in the liquid condition; many hundreds of thousands of tons of liquid fats, such as whale oil, cotton-seed oil, and others, are now converted annually into semi solid or solid fats suitable for incorporation in edible fats (butter substitutes or cooking fats) and for use in the manufacture of soap. Before dealing further with the subject of fat-hydrogenation, individual mention may be made of other examples of hydrogenation which have become of some technical importance: the hydrogenation of naphthalene and of phenols in the liquid state under pressures of hydrogen from 5 to 50 atm. by means of nickel at about 180°, furnishing respectively *tetra* and *deca hydronaphthalenes* (solvents), and cyclo*hexanols* or cyclo*hexanones* (solvents and also employed in soaps); the conversion of crotonaldehyde into butyl alcohol, of acetone into *isopropyl alcohol*, and of acetaldehyde into *ethyl alcohol*, by hydrogen in presence of nickel at 140°; the production of certain *synthetic* perfumes, notably *menthol* from thymol or piperitone, and *citronellol* from citral or geraniol (nickel at 140°–180°).

Fat-hydrogenation.—This is usually carried out at about 180°, with hydrogen either at atmospheric pressure or at pressures not exceeding 5 atm. (usually about 2 atm.). For

fat-hardening the hydrogen is usually made by the intermittent steam-iron process, when it contains only traces of carbon monoxide; electrolytic hydrogen is also frequently employed. The fatty oils may be refined by alkali neutralisation followed by bleaching with adsorbent earth, and should be as free as possible from oxidised oils or other material toxic to the catalyst. The oils are mixed with a small proportion of catalyst (0·1–1% of nickel on the fat) and then either agitated vigorously in a closed vessel whilst a current of hydrogen is continuously passed through the liquid, or sometimes the mixture of fat and catalyst is sprayed into closed vessels filled with hydrogen. With fats of good quality the desired hardening is usually attained in the course of 2–3 hours. After removal from the hydrogenated fat by filtration, the catalyst can be re-used several times on fresh batches of oil before its activity becomes too much reduced by accumulation of catalyst poisons, etc. Nickel-kieselguhr catalysts are very widely used; nickel carbonate is precipitated upon kieselguhr, the product is thoroughly washed, dried, and then reduced in hydrogen at 300°–500° and stored either in an inert atmosphere or under the fatty oil itself. Alternatively, nickel formate is reduced under the oil at 240°; this temperature is higher than is desirable in the hydrogenation of the fat and, therefore, a quantity of the formate is reduced in a portion of the oil, and the product cooled to about 170° and diluted with more of the fat prior to its hydrogenation at the latter temperature. When nickel prepared from the formate is employed (as in a number of fat-hardening plants recently installed), it is subsequently removed by filtration through a bed of kieselguhr, or kieselguhr may also be added to the fat initially. In the absence of kieselguhr it is difficult effectively to remove the colloidal nickel suspension from the oil.

An alternative and continuous process of fat-hydrogenation is that in which the liquid trickles downwards over a mass of activated nickel turnings in an atmosphere of hydrogen. The catalyst is, in this case, stationary; it is made active in the first instance by anodic oxidation of the nickel turnings, followed by reduction of the superficially deposited layer of nickel oxide. When the activity of the catalyst declines, it can be regenerated by further anodic oxidation and subsequent reduction. The continuous process is also applied to the vapour or liquid hydrogenation of naphthalene, phenols, pyridine, and acetone.

Fatty Alcohols from Fats.—When fats are agitated with hydrogen as described above, but at high pressures (5–100 atm.), at 250°–300°, and in presence of a reduced basic copper chromate ("copper-chromite") catalyst instead of nickel, the acidic groups are almost quantitatively reduced to alcohols:

$$RCOOH \longrightarrow RCH_2OH$$

This method is now adopted on a large scale for the manufacture of higher fatty alcohols from selected natural fats. The alcohols in question, especially dodecyl, hexadecyl (cetyl), and oleyl alcohols, yield sulphuric acid mono-esters, the alkali salts of which have very useful detergent, emulsifying, dispersing and/or wetting-out properties; many higher alkyl sodium sulphates are now available and find use in the textile industries and as components of shaving creams, shampoos, and other toilet and household detergents.

Oxidation.—Many processes of oxidation in organic compounds are also induced, accelerated, or retarded by catalysts. An example of the latter, negative type of catalysis is the addition of small proportions of "antioxidants" to fats, rubber, and some other materials in order to delay the onset of atmospheric oxidation.

In the manufacture of aldehydes or ketones from alcohols, processes of oxidation or dehydrogenation may be employed singly, or in combination. Thus, *formaldehyde* is usually produced by controlled oxidation of a mixture of methyl alcohol vapour and air submitted to a short contact with heated copper or silver gauze; but it has been stated that, by using less air than in the usual process, the yield of formaldehyde can be notably increased, part being formed by oxidation, the remainder by dehydrogenation ($CH_3OH \rightarrow CH_2O+H_2$). Since the latter action requires heat, whilst the oxidation is a strongly exothermal action, the process becomes more efficient if both processes can go on concurrently. In the conversion of ethyl alcohol into *acetaldehyde* the conditions are to some extent reversed: direct oxidation cannot be efficiently carried out, but passage of alcohol vapour over catalytic copper at 300° results in about 25% conversion of alcohol into hydrogen and acetaldehyde in almost theoretical yield. This process has been used for the technical production of acetaldehyde, which is now a most important intermediate stage in the manufacture of many aliphatic solvents (*v.* acetaldehyde); but it has subsequently been found that the addition of sufficient air to oxidise about 35% of the alcohol, and passage of the mixed gases over a short layer of copper or silver catalyst at 450°, results in about 85% conversion of the alcohol to acetaldehyde. In this form the manufacture of aldehyde from alcohol is now carried out on a large scale in this country and elsewhere. Cyclic alcohols, such as *cyclo*hexanol or borneol, are readily dehydrogenated by copper at 300°, to give the corresponding ketones.

Acetaldehyde itself is readily oxidised to *acetic acid* by the action of a current of air and in presence of dissolved manganese acetate, which catalyses the decomposition of the explosive peracetic acid ($CH_3{\cdot}CO_3H$), which is produced by the initial combination of acetaldehyde and oxygen. Acetic acid is technically produced for the most part by this process (*v.* acetic acid).

The most notable recent development in technical catalytic oxidation of organic compounds is the oxidation of the latter in the vapour state by air in presence of vanadium pentoxide as catalyst. The oxide, mounted on iron or aluminium pellets, was first used in this connection in the partial oxidation of aromatic hydrocarbons by air. Since the desired products are intermediate in stability between the original compounds and the ultimate products

of oxidation, the conditions of technical operation (especially temperature control, the actions being strongly exothermic) have demanded much skill, but the method has proved extremely successful *Phthalic anhydride* is now very largely obtained from naphthalene by this method of oxidation, and *anthraquinone* is also produced either by similar direct oxidation of anthracene, or indirectly from naphthalene through phthalic anhydride and *o* benzoylbenzoic acid. Catalytic oxidation of toluene furnishes *benzaldehyde* and *benzoic acid*, whilst *malic acid* (used in flavouring materials as a substitute for citric or tartaric acids) is obtainable from benzene as starting material. Benzene yields first *p* quinone and then *maleic anhydride* when passed with air over vanadium oxide at about 400°; the yield of the anhydride is over 50% by weight of the benzene consumed, and malic acid results when it is heated under pressure with water

HYDRATION AND DEHYDRATION.—The production and hydrolysis of esters or ester like compounds are among the most familiar examples of reactions in which catalytic action plays an important part. Instances of industrial uses of catalysis in hydrolytic actions include the manufacture of crystalline glucose and sugar syrup from potato, maize, or other starch, the hydrolysis of fats into free fatty acids and glycerol by the Twitchell hydrolytic agent or its later analogues (essentially condensation products of, for example, an aromatic sulphonic acid with oleic or other fatty acid, the active agent thus containing in its molecule a strongly hydrophilic group and a long hydrocarbon chain system), the acid hydrolysis of fats, the action of iron salts in promoting the conversion of benzylidene chloride into benzaldehyde, and benzotrichloride into benzoic acid, when heated with water or milk of lime; and the proposed use of concentrated or gaseous hydrochloric acid in order to convert waste cellulose materials into fermentable sugars.

In the converse process of esterification, the use of mineral acid catalysts is familiar in the manufacture, from the respective alcohols and acids, of such compounds as ethyl, amyl or benzyl acetate, methyl or ethyl benzoate, methyl and amyl salicylates, ethyl succinate, lactate or phthalate, etc. Similarly, the action of anhydrous sodium acetate or similar catalyst in promoting acetylation is taken advantage of in the manufacture of products such as acetyl salicylic acid and many other medicinal and other compounds, while the production of cellulose acetate involves the use of appropriate catalytic aids to acetylation.

The dehydration of alcohols to olefines or ethers is another important application. Ethyl ether is manufactured by a continuous process from alcohol by heating the latter with the correct proportion of sulphuric acid at about 130°, while, when required, ethylene can be produced by similar means (preferably with syrupy phosphoric acid as catalyst), or by passage of alcohol vapours over alumina at 360°. The hydration of olefines to the corresponding alcohols by absorption in sulphuric acid and subsequent hydrolysis of the resulting alkyl hydrogen sulphates has been the subject of technical research, both as regards the ethylene present in coke oven gas and the lower olefines present in "cracked" petroleum gases. Processes for the conversion of the latter into propyl, butyl, amyl and hexyl alcohols have been worked out in America, both by means of absorption in sulphuric acid and of combination with hydrogen chloride to give the corresponding alkyl chlorides, and in both cases it has been observed that the processes involved can be accelerated in presence of suitable catalysts.

For the catalytic hydration of acetylene to acetaldehyde, and for the preparation of organic solvents from acetaldehyde, alcohol, or acetylene *see* ACETYLENE.

ADDITION AND SUBSTITUTION OF HALOGENS—The use of chlorine or other halogen "carriers" is one of the oldest instances of catalytic action in technical organic chemistry. The employment of such catalysts has been much extended in the present day manufacture of many inorganic and organic compounds. (It may be added here that the manufacture of chlorine itself, by the Deacon or Hargreaves Robinson processes, was also an early instance of large-scale practice of catalytic methods, but these have, of course, fallen into disuse with the advent of electrolytically produced chlorine)

Activated charcoal has proved of great service as a catalyst in the manufacture of several inorganic halogen compounds, especially *phosgene*, $COCl_2$, and *sulphuryl chloride*, SO_2Cl_2, it has also been used to effect the combination of electrolytic hydrogen and chlorine in the manufacture of *hydrochloric acid*, but in modern practice this is achieved more simply by burning chlorine in an atmosphere of hydrogen *Hydrobromic acid*, on the other hand, has been made technically by passage of bromine vapour and steam over active charcoal at 500°.

Other well-known cases of catalytic addition or substitution of halogens are the uses of anhydrous ferric chloride in the chlorination of benzene or toluene, of sulphur, phosphorus, or iodine in the production of monochloroacetic acid, and of antimony pentachloride in the production from acetylene of tetrachloroethane and thence of trichloroethylene (Westrosol), used as a non inflammable solvent and dry cleaning agent.

OTHER CATALYTIC PROCESSES.—Much space would be required if an attempt were made to illustrate all the other kinds of reactions of organic compounds which are favourably influenced by catalysts, and it must suffice merely to indicate the employment of these agents in connection with the following operations: the preparation of aromatic hydrocarbons, *e g* of toluene by the action of methyl chloride on benzene in presence of aluminium chloride; the preparation of sulphonic acids derived from benzene and other hydrocarbons, from pyridine, etc.; the preparation of derivatives of amines or of amino-compounds, particularly of those in which aromatic radicals are introduced into the amino-group, *e g.* the production of phenyl anthranilic acid, which is easily effected by the addition of a small quantity of copper powder to a boiling solution of *o*-chlorobenzoic acid in aniline; the preparation of certain diazo

compounds, and the replacement of the diazo-group by the chlorine, bromine, or cyanogen radical; many condensation reactions in which small proportions of sodium ethoxide, pyridine, piperidine, and other compounds exert catalytic action; the preparation of certain sulphur compounds, in which category the important methods of vulcanising rubber may be included. Moreover, in many cases, intramolecular re-arrangements and polymerisations are accelerated by catalysts. The transformation of hydrazobenzene into benzidine under the influence of a strong acid is a familiar example of the former class of change, whilst the latter is exemplified in the synthesis of various kinds of rubber by the polymerisation of butadiene and its homologues, which is promoted by the presence of sodium, acetic acid, and other catalysts. Another instance of catalytic polymerisation is afforded by recently developed processes wherein the olefines (propylene, butylenes, butadienes, etc.), present in gases from cracked petroleum, are passed under pressure over heated phosphoric acid or cadmium phosphate and converted into low-boiling liquid hydrocarbons.

Reference should also be made to many electrolytic processes, *e.g.* the preparation of hypochlorites, chlorates, and persulphates, in which advantage is taken of the presence of small amounts of an appropriate catalyst in the electrolyte.

Fermentation Processes.—Finally, it must be noted that a number of very important operations, for example, the manufacture of ethyl alcohol, are carried out through the agency of that group of catalysts produced by living organisms which are known as enzymes. In many respects the action of enzymes is similar to that of inorganic catalysts, and especially to that of colloidal platinum or palladium, but is specific in the sense that a definite enzyme is required to bring about a particular transformation.

The ordinary alcoholic fermentation of sugar by yeast is profoundly modified when conducted in presence of sodium sulphite or carbonate in suitable dilution; under these conditions acetaldehyde, which is an intermediate stage in the formation of alcohol, is removed from the sphere of action, and glycerol, which normally is present in only small amounts in the products of fermentation, accumulates owing, ultimately, to lack of acetaldehyde to serve as an acceptor for hydrogen. The process has been operated successfully, when economic considerations permitted, for the manufacture of glycerine from beet-sugar or molasses.

Certain improvements have been effected in the lactic acid and butyric acid fermentations of sugar, and in the production of citric acid by moulds and of acetic acid (vinegar) from alcohol. The most striking new procedure in sugar fermentation is, however, the use of cultures of specific bacteria (*Granulobacter*, *Clostridium* sp.) which convert glucose into *n*-butyl alcohol, acetone, hydrogen, and carbon dioxide. This process is operated on a very large scale in America, primarily for butyl alcohol, which is in great demand as a basis for solvents; acetone is at present a useful by-product, and in at least one factory the fermentation gases are compressed and converted into methyl alcohol by high-pressure hydrogenation with zinc-chromium oxides (*v. supra*).

Reference may also be made here to acid hydrolysis processes for the conversion of celluloses and starches into fermentable sugars, to suggested processes for the manufacture of acetic and other acids from cellulose waste. and to the established, although not very widely worked, method of hydrolysis (splitting) of fats by castor-seed lipase. T. P. H.

CATAPLEIITE. Hydrated silicate and zirconate of sodium and calcium, containing ZrO_2 30–40%. The crystals are yellow and have the form of thin hexagonal plates; sp.gr. 2·8, H. 6. It occurs with other rare minerals in nepheline-syenite on the islands in the Langesund-fjord in south Norway, and at Narsarsuk in Greenland. L. J. S.

CATECHIN *v.* Catechu or Cutch.

CATECHOL (*Pyrocatechol*, o-*Dihydroxybenzene*, *1:2-Phendiol*, $C_6H_4(OH)_2$). First isolated by von Reinsch in 1839 from the distillation of catechu, crystallises in colourless prismatic needles or tablets, m.p. 105°, b.p. 245°, and is readily soluble in water, alcohol, ether, benzene, and alkalis; it sublimes, and is volatile in steam. An aqueous solution reduces silver nitrate in the cold and Fehling's solution on warming; with ferric chloride it gives a green colour which turns violet on addition of ammonia or sodium acetate (Hlasiwetz and Barth, Annalen, 1864, **130**, 353; Wislicenus, *ibid.* 1896, **291**, 174) whilst Bayer reports that the test is more sensitive in the presence of aromatic amino-sulphonic acids when a red-brown colour develops (Biochem. Z. 1909, **20**, 178). An ammoniacal solution of calcium chloride precipitates the calcium salt, and lead acetate yields the lead salt. An alkaline solution becomes green, then black on exposure to air.

Ekkert (Pharm. Zentr. 1926, **67**, 566) detects catechol by the addition of 0·5 c.c. of an aqueous solution to 4 c.c. of concentrated sulphuric acid containing 0·02 g. sodium nitroprusside when a green upper layer results and on mixing and dilution with water the solution becomes red, turning to green with ammonia. An alkaline solution of sodium nitroprusside yields an intense green colour which changes to bluish-green with acetic acid (Pavolini, Boll. Chim. farm. 1930, **69**, 713, 719) whilst a boiling ammoniacal solution of catechol with a small quantity of nitroprusside gives a cherry red colour (Sivadjian, J. Pharm. Chim. 1931, **13**, [8], 529). As little as 0·000012 g. of catechol in 1 c.c. of solution may be detected by the reduction of *o*-dinitrobenzene in the presence of sodium carbonate to a deep violet quinonoid salt (Bose, Amer. Chem. Abstr. 1933, **27**, 5682); with phosphomolybdo-tungstic acid a red-violet colour is produced which turns to blue (Bezssonov, Bull. Soc. Chim. biol. 1922, **4**, 83) and with ammonium molybdate solution together with acetic acid a reddish-brown colour results, this arising with all *o*-hydroxy aromatic compounds (Quastel, Analyst, 1931, **56**, 311). Quantities down to 7×10^{-7} mol. may be detected colorimetrically by the reduction of ferric iron

in an alkaline medium in the presence of sucrose (Schmalfuss, Spitzer, and Brandes, Biochem. Z. 1927, 189, 226), whilst Blazsó (Chem. Zentr. 1933, i, 952) describes the microdetermination of catechol by its oxidation with 0·01N-alkaline ferrocyanide, excess of which is reduced with potassium iodide in the presence of acetic acid and zinc sulphate; the reaction is not stoichemetric and conditions must be standardised. Catechol may be estimated even in the presence of hydroquinol, resorcinol, or phenol by precipitation as the lead salt (Degener, J. pr. Chem. 1879, [ii] 20, 320, Bock and Lock, Monatsh. 1929, 53–54, 888). For its detection in the presence of resorcinol and other compounds, *see* Jones, Prahl, and Taylor (Ind. Eng. Chem. [Anal.], 1932, 4, 84), and Rossi (Amer. Chem. Abstr. 1924, 18, 2293).

Catechol occurs widely in plants and vegetables, sometimes free as in onion scales (Link and Walker, J. Biol. Chem 1933, 100, 379) but more often in combination as tannins. It is found in many coals, in cellulose waste liquors (Swedish Pat. 62831 and 54200), in gasworks liquor (Key and Etheridges and Eastwood, Gas J. 1933, 204, 506, 882, 1934, 208, 354; G.P. 532178; U.S.P. 1821815), in wood tar (Ugriumiov, 1935, A, 1028), and in the tar water of bituminous shale, G.P. 68944). As the sulphate it is found in the urine of man and herbivorous animals (Müller, Ber. 1874, 7, 1526, Schmiedeberg, Z. physiol. Chem. 1882, 6, 189).

It is formed in the dry distillation of many tannins and their derivatives, and may be obtained by the destructive distillation of leather scrap (Michelman, Ind. Eng. Chem. 1925, 27, 247; Meier, Amer. Chem. Abstr. 1929, 23, 2319), while many other natural products such as paper and sugar yield smaller amounts.

Catechol may be prepared from guaiacol in almost theoretical yield by treatment with fuming hydriodic acid (Perkin, Proc. Chem. Soc. 1890, 90) or in 70% yield by heating to 210° with aluminium chloride (Hartmann and Gattermann, Ber. 1892, 25, 3532). *o*-Bromo- or *o*-chlorophenol when fused with alkali gives catechol (G.P. 84828), but the yields are poor owing to its instability with the strong alkali. A continuous process with good yield is claimed in B.P. 425230 and 432276, *o*-dichlorobenzene being heated (at 250°–300° in an autoclave) with aqueous baryta or strontia together with a copper catalyst and a reducing agent sufficient to destroy any oxygen present. Not more than 50% catechol can be obtained from the fusion of phenol-2-4 disulphonic acid ("α phenoldisulphonic acid") with caustic alkali at 280°–300° in an autoclave (B.P. 21853; G.P. 80817); catechol monosulphonic acid is formed and is hydrolysed by heating with 50% sulphuric acid to 180°–220° under pressure. A similar process is claimed by Tobias (G.P. 81210), who obtained catecholdisulphonic acid from alkali fusion of phenoltrisulphonic acid and then hydrolysed the former to catechol. Other similar but less direct methods are described by Heyden and Hähle (G.P. 69116 and 60637), Mannet (G.P. 97099), Messel (G.P. 68944) and Cross, Bevan and Heiberg (Ber. 1900, 33, 2018). The direct oxidation of phenol by sodium peroxide to give 25% catechol is detailed by Magidson, Posorovskaja, and Seligsohn (1928, A, 516).

The most satisfactory commercial preparation is provided by the action of alkalis on *o*-chloro- or *o*-bromo-benzene (*v. supra*, and G.P. 269544 and 249939), yields up to 90% being claimed. The oxidation of salicylaldehyde provides a convenient laboratory method of preparation, an alkaline solution being treated with 3% hydrogen peroxide (Dakin, Amer. Chem. J. 1909, 42, 477; and Organic Syntheses, III, 27). A yield of about 70% is thus obtained.

The heat of combustion of catechol at constant pressure is 684·9 kg.-cal. per g.-mol (Barker, J. phys. Chem. 1925, 29, 1345). Weissenberger, Henke, and Bregmann (Monatsh. 1926, 46, 471) give vapour pressures, surface tensions, and viscosities of solutions in alcohol, ether, and acetone. The specific heat has been measured by Andrews (J. Amer. Chem. Soc. 1926, 48, 1287), who arrived at the formula:

$$Cp=1 \cdot 3+0 \cdot 1074T$$

From the experiments of Bourion and Tuttle (Compt. rend. 1928, 186, 1124) it is concluded that an equilibrium between single and triple molecules exists in solution, the heat of association being −2,400 g.-cal. per g. Sarkar (Phil. Mag. 1926, 2, [7], 1153) describes X-ray powder photographs of catechol from which the space grouping is obtained.

Hagemann (Z. angew. Chem. 1929, 42, 355; 1931, 44, 226) claims up to 56% yield of butadiene on pyrolysing catechol in a hot tube in the presence of nitrogen.

Reduction of catechol to a mixture of 75% phenol, 10% benzene, and 15% resin by hydrogen and an alumina copper oxide catalyst is described by Ipatiev and Orlov (Ber. 1927, 60, [B], 1963), while Packendorff (Ber. 1935, 68, [B], 1251) obtained *cyclo*hexane and *cyclo*hexanol with hydrogen and a platinum oxide catalyst in ethyl acetate at room temperature.

Catechol, like other *o*-hydroxy compounds, readily forms complexes with acetone (Baker, J.C.S. 1934, 1678; Boeseken and Slooff, Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 534). It readily combines with boric, arsenic, and other acids and acidic salts to give compounds yielding series of salts with metals, many of which are used in chemotherapy and as bactericides. Thus Weinland and Maier (Z. anorg. Chem. 1926, 150, 217) discuss the structure of the barium and calcium catechol stannates obtained by the addition of the metal acetates to catechol and stannic chloride in water. With arsenic acid in boiling water catechol yields tricatecholarsenic acids, a stable solid yielding stable salts with metallic oxides or hydroxides (Weinland and Heinzler, Ber. 1919, 52, [B], 1321; G.P. 557726); their constitutions are discussed by Rosenheim and Plato (Ber. 1925, 58, [B], 2000) and Reihlen, Sapper and Kall (Z. anorg. Chem. 1925, 144, 218). Catechol also yields complexes with molybdic acid (Weinland and Gaisser, *ibid.* 1919, 108, 238), with antimony trioxide and alkali (G.P. 606431), with alkaline earth salts (Scholder and Wolf, *ibid.* 1933, 210, 184, Scholder and Schletz, *ibid.* 1933, 211, 161), with iron salts (Weinland and Binder, Ber. 1912,

45, 152, 1118), with cobalt salts (Weinland and Döttinger, Z. anorg. Chem. 1918, **102**, 234), and with organic acid salts (Weinland and Denzel, Ber. 1914, **47**, 2247, 2993). For an extensive discussion of the chemical properties and colours of the complexes with iron, cobalt and nickel, *see* Reihlen (Z. anorg. Chem. 1922, **123**, 173). Spacu and Kuraš (J. pr. Chem. 1934, [ii.] **141**, 201) suggest formulæ for metallic pyridine complexes.

Catechol is used in photography, forming a very efficient developer in the presence of an accelerator such as sodium sulphite or sodium phosphate (Eder, J.S.C.I. 1890, **9**, 102 ; Brit. Phot. 1900, **47**, 676). Full details for its use and formulæ for different stock solutions are given by McClintash (Brit. J. Phot. 1923, **70**, 623). A large number of valuable derivatives are also obtained from catechol.

Its bactericidal action is compared with that of phenol and of many other compounds by Sabalitschka and Tietz (Arch. Pharm. 1931, **269**, 545). The pharmacology and physiological action are treated by Tainter (J. Pharmacol. 1930, **40**, 43), Mulinos and Osborne (Proc. Soc. Exp. Biol. Med. 1935, **32**, 1344), Barrenscheen and Danzer (Z. physiol. Chem. 1933, **220**, 57), and by Hefftner in Ellenger's "Handbuch der experimentalen Pharmakologie," Band I, p. 941, Berlin, 1923. A detailed pharmacology of catechol phosphate is given by Smith, Engel, and Stohlmann (Amer. Chem. Abstr. 1933, **27**, 3253).

Catechol yields an orange-yellow *picrate*, m.p. 122° (Baril and Hauber, J. Amer. Chem. Soc. 1931, **53**, 1087) and a di-m-*nitrobenzoate*, m.p. 144° (Meijer, Rec. trav. chim. 1934, **53**, 387). It may be rapidly and quantitatively *acetylated by adding acetic anhydride to a* solution in aqueous caustic alkali (Chattaway, J.C.S. 1931, 2495). Methylation can be effected by the usual methods and Tanaka, Ishimasa, and Koyama (Amer. Chem. Abstr. 1926, **20**, 2670) compare the efficiencies and relative amounts of guaiacol and veratrol produced in the various methods.

Ethers and Esters.

Monoethyl catechol ether is guaiacol.

Dimethyl catechol ether is veratrol.

Diethyl catechol ether, m.p. 43°–45°, is obtained by the action of ethyl iodide and alcoholic KOH on catechol (Herzig and Zeisel, Monatsh. 1889, **10**, 152).

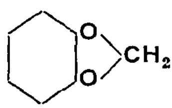
Monophenyl catechol ether, m.p. 107°, is volatile in steam and may be prepared by boiling a benzene solution of 2-methoxydiphenyl-catechol ether with aluminium chloride (Ullmann and Stein, Ber. 1906, **39**, 623) or by the interaction of benzene diazonium chloride with catechol (Norris, Macintire and Corse, J. Amer. Chem. Soc. 1907, **29**, 127).

Phenylmethyl catechol ether, m.p. 77°, results when the potassium compound of guaiacol is heated in guaiacol with chlorobenzene at about 220° (G.P. 269543).

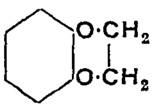
Diphenyl catechol ether, m.p. 93°, is described by Ullmann and Sponagel (Annalen, 1906, **350**, 96), who obtained it by the action of potassium and copper powder on *o*-dibromobenzene and phenol at 220°–250°.

The properties of many *catechol monoethers* are given by Klarmann, Gates, and Shternov (J. Amer. Chem. Soc. 1932, **54**, 1204), who also compare their bactericidal powers.

Methylene catechol ether (I), a colourless liquid, b.p. 172°–173°, is prepared by heating for 20 hours



I.



II.

catechol and methylene-chloride with sodium ethoxide at 120°. *Ethylene catechol ether*, (II.) b.p. 212°–214°, is prepared by 7–8 hours' heating at 190°–200° of a mixture of catechol, ethylene bromide, copper powder, and glycerol (Ghosh, J.C.S. 1915, **107**, 1597).

These and other cyclic ethers (*e.g.* vinyl, methyl vinyl ethers, etc.) yield bromo-, chloro-, etc., derivatives by suitable treatment (Ghosh, *ibid.* ; Orr, Robinson and Williams, J.C.S. 1917, **111**, 949 ; Moureu, Compt. rend. 1898, **126**, 1426).

Catechol hydrogen carbonate,

$$C_6H_4(OH){\cdot}O{\cdot}CO_2H,\tfrac{1}{2}H_2O,$$

m.p. 240°, is produced when ammonium carbonate is heated with catechol at 130°–140° under pressure or when catechol is heated at 180°–210° with glycerol and potassium bicarbonate in carbon dioxide (Praxmarer, Monatsh. 1906, **27**, 1199.) Esters of this acid and compounds formed by it with bases are used in medicine (Einhorn, G.P. 92535).

Catechol carbonate, m.p. 118°–120°, may be prepared by treatment of catechol with diphenyl carbonate at 250° (Bischoff and von Hedenström, Ber. 1902, **35**, 3435) or by the interaction of phosgene and catechol in alkaline solution (Einhorn and Lindenberg, Annalen, 1898, **300**, 141 ; G.P. 72806). It may be nitrated by fuming nitric acid to 4-nitrocatechol carbonate, and this compound then furnishes a source of the 4-*nitrocatechol* (G.P. 264012 ; *v. infra*).

Catechol monoacetic acid,

$$C_6H_4(OH)O{\cdot}CH_2{\cdot}CO_2H$$

m.p. 131°, is obtained by the action of monochloracetic acid on catechol in alkaline solution (G.P. 87336, 87668, 89593). It may be purified by conversion on heating to 120° to its anhydride, m.p. 56°. Salts and derivatives are used therapeutically (Boruttau, Chem. Zentr. 1919, III, 832).

Bischoff and Fröhlich (Ber. 1907, **40**, 2780) describe *catechol diacetic acid*.

Catechol diacetate, needles, m.p. 63·5°, is easily obtained from catechol and acetyl chloride at room temperature (Nachbaur, Annalen, 1858, **107**, 246 ; Sudborough and James, J.C.S. 1905, **87**, 1756).

Catechol acetate methyl ether, guaiacyl acetate, "*Eucol*," b.p. 239°–241°, is prepared from guaiacol and acetic anhydride with a very little sulphuric acid (Biscaro, Chem. Zentr. 1907, I, 745).

Alkyl Derivatives.

Alkyl catechols may be readily prepared by condensation of catechol with acid chlorides or with acids in the presence of a condensing agent,

Fries rearrangement of the ester so formed and subsequent Clemmensen reduction of the *acyl-catechol*. Rosenmund and Lohfert (Ber. 1928, 61, [B], 2601) find that di-esters of catechol rearrange in hot nitrobenzene containing aluminium chloride, one acyl group migrating chiefly to the 4-position and the other splitting off. The best yields are obtained in general by heating the di-ester and aluminium chloride for 2 hours at 75° together with 1 mol. of catechol; in this way an 88 0% yield of 4 *acetocatechol* or a 70 0% yield of 4-*butyrocatechol* was obtained B P. 317194 claims the preparation of *acyl* derivatives of *monoalkyl catechols*, used as therapeutic agents, by the condensation of an aliphatic acid chloride with a monoalkyl ether of catechol in the presence of 2 mols. of aluminium chloride; the acyl group takes up the *p*-position to the —OH and the ketone may be reduced by the Clemmensen method.

4 *Caproylcatechol* (yield 62%, m.p. 93°–94°) and 4-*hexoylcatechol* (yield 50%, m.p. 25°–26°) are obtained from catechol, and 10% excess of the acid chloride followed by the same rearrangement (Stoughton, Baltzly, and Bass, J. Amer. Chem Soc. 1934, 56, 2007). The condensation of octoic acid with catechol in the presence of zinc chloride at 125°–135°, and subsequent Clemmensen reduction to *β ethylhexylcatechol* is described in U S P. 1974821, germicidal and therapeutic properties are claimed for the product.

Catechol ethers readily undergo rearrangement to alkyl catechols. Thus Perkin and Trikojus (J C.S 1927, 1663) prepared 4 *allylcatechol* (m p. 48°), identical with the "allylcatechol" isolated from Java betel leaf oil, together with 3-*allylcatechol* (m p. 28°) by the rearrangement of the monoallyl ether of catechol at 170°–180°. Kawai (Amer. Chem. Abstr. 1926, 20, 1798) and Hurd, Greengard and Pilgrim (J. Amer. Chem. Soc. 1930, 52, 1700) describe the same reactions and the latter showed that *diallyl ether* of *catechol* yields 3.6 *diallylcatechol* on rearrangement.

Rohm and Haas Co. (U.S P. 2008032, 2008095) treat catechol with diisobutylene and sulphuric acid or aluminium chloride to give products of high bactericidal properties The material, m p about 110°, is suggested as a germicide or as raw material in dye and allied industries.

Alkyl catechols may also be prepared by hydrolysis of *chloroalkyl catechols*. 4-*Phenyl-catechol* is made from 4 phenyl 2-chlorophenol by heating with an aqueous solution of alkali metal hydroxide or carbonate to above 200° (U.S.P. 1952755).

4-*Butyl-* and 4-*amyl catechol*, prepared by hydrolysis of 2-halogeno-4 alkyl catechols in the presence of cuprous oxide, are suggested as stabilisers for insecticidal compounds, as antioxidants for fats, soaps, etc, and to prevent gum formation in petrol fuels (U.S.P. 1912827).

Allyl-, *acyl-*, and *aryl catechols* have been widely used as therapeutic antiparasitic agents, germicides, and in other ways. Lamson, Brown, and Ward (J. Pharm. Exp. Ther. 1935, 53, 198) conclude that 4 *hexylcatechol* is the only polyhydroxy-benzene homologue to exert marked ascaricidal properties, but many claims for other similar catechols occur in the patent literature.

Nitro Derivatives.

3 *Nitrocatechol*, m.p. 86 5°, may be obtained by the direct nitration of catechol in ether by fuming nitric acid (Weselsky and Benedikt, Monatsh. 1882, 3, 386) when it is most easily separated from the 4-*nitrocatechol* also formed by extraction with petrol in which the 3 nitrocatechol is the more soluble (Vermeulen, Rec trav. chim. 1906, 25, 23; Foglesong and Newell, J. Amer. Chem. Soc. 1930, 52, 834); *m* nitro- and *m*-amino phenol on oxidation also yield 3 nitrocatechol (Bamberger and Czerkis, J. pr. Chem. 1903, [ii], 68, 477).

4-*Nitrocatechol*, m p. 175°, obtained together with the 3 nitro compound as above, is also prepared by the oxidation of *m*-nitrophenol with potassium persulphate in alkaline solution (G P. 81298) Cardwell and Robinson (J C S 107, 258) prepared 4-nitrocatechol by hydrolysing 4 nitrocatechol 2 methyl ether with hydrobromic acid It is also obtained by nitrating catechol carbonate (*v supra*) with fuming nitric acid and heating the product with water (G P. 264012) van Erp (Ber 1931, 64, [B], 2813) describes the hydrolysis of 2-chloro 4 nitrophenol with aqueous potash to give 4 nitrocatechol; caustic soda is not satisfactory.

3 5-*Dinitrocatechol*, m p 164°, is formed when catechol diacetate is nitrated with concentrated acid and the product hydrolysed with cold sulphuric acid (Nietzki and Moll, Ber. 1893, 26, 2183).

Sulphonic Acids.

Catechol sulphonic acid is best prepared by hydrolysis of a *m*-halogen phenol sulphonic acid by caustic soda at temperatures above 200° (*inter al.*, G.P. 9623; B P. 14931).

Catechol 3 5 *disulphonic acid* is obtained by direct sulphonation of catechol with fuming sulphuric acid (Cousin, Compt. rend. 1893, 117, 113) or by fusing phenol trisulphonic acid or its salts with alkalis.

Both the sulphonic and disulphonic acids find much use either alone or as salts or complexes in chemotherapy especially as vermifuges Schmidt (Chem. Zentr. 1934, i, 3878) details the use of the sodium salt of catechol 3 5 disulphonic acid (I) in the preparation of complexes for medical use. *Fuadin*, Sb'''—bis—(I)·$7H_2O$, and *Stiadin*, Ca—(I) $4H_2O$, are compared with tartar emetic for pharmacological and therapeutic use (*see also* J. Amer. Med. Assoc. 1933, 100 1635). The preparation of these and other complexes are covered in U.S.P. 879533, 1889383, 1718492. Erhardt and Brumpt (Amer. Chem Abstr. 1933, 27, 3003) show that cat liver flukes are not killed by fuadin and other antimony compounds. Arsenic, mercury and manganese *complexes are particularly active* in causing increased excretion of eggs but are less active than the antimony compounds and do not kill the worms.

Halogen Derivatives.

4 *Chlorocatechol*, m.p. 80°–81°, is obtained by the action of sulphuryl chloride on catechol in ether; some 3 *chlorocatechol* is also formed (Paratoner, Gazzetta, 1898, 28, I, 22?). Two

modifications, m.p. 90°–91° and 59°–61°, have been isolated.

4:5-*Dichlorocatechol*, m.p. 116°–117°, is formed if excess sulphuryl chloride is used in the above reaction or if 4-chlorocatechol is treated with sulphuryl chloride (Paratoner, *l.c.*).

3:4:5-*Trichlorocatechol*, m.p. about 106°–109°, is obtained by the action of chlorine on 4:5-dichlorocatechol in acetic acid (Willstätter and Müller, Ber. 1911, **44**, 2185).

3:5-*Dichlorocatechol*, m.p. 83°–84°, results from the oxidation of 3:5-dichlorosalicylaldehyde with alkaline hydrogen peroxide (Dakin, J. Amer. Chem. Soc. 1909, **42**, 488).

For the preparation of 4-*bromo-* and 3:5-*dibromocatechol*, *see* Dakin (*l.c.*).

3:4:5-*Tribromocatechol* is obtained in good yield by the direct bromination of catechol in chloroform (G.P. 207544, 215337) whereas *tetrabromocatechol* results from the action of excess bromine on 6-bromopiperonal for 3 hours at 100° in the presence of 1% of aluminium bromide (Raiford and Oberst, J. Amer. Chem. Soc. 1933, **55**, 4288).

The preparation of 4-*iodocatechol* from 4-aminocatechol diacetate is detailed by Fourneau and Druey (Compt. rend. 1934, **199**, 870).

Catecholphthalein is prepared by heating 3 parts phthalic anhydride with 2 parts of catechol and 3 parts zinc chloride to 140°–150° for 3–4 hours. It may be crystallised from benzene but has no sharp melting-point, sintering at 80°–90°. The yellowish crystals are volatile in steam, dissolve in cold concentrated sulphuric acid to give a deep red solution, are soluble in caustic alkali to give a faintly fluorescent blue and in mild alkali to give a violet solution.

Catecholitaconein and **catecholcitraconein** are described by Dhar and Dutt (J. Indian Chem. Soc. 1927, **4**, 247).

For dyes produced from catechol and diazo-compounds, see Witt and Mayer (Ber. 1893, **26**, 1072) and Orton and Everatt (J.C.S. 1908, **93**, 1010).

With phthalic anhydride and sulphuric acid at 150°, catechol yields alizarin (Liebermann and Hohenemser, Ber. 1902, **35**, 1778) (*v.* ALIZARIN).

Helferich, Lang and Schmitz-Hillebrecht (J. pr. Chem. 1933, ii, **138**, 275) describe *glucose-azodyes* of catechol which dye wool a reddish-yellow at 100° or in the presence of emulsin.

CATECHU or CUTCH. There are several varieties of catechu or cutch bearing different names according to the country or plants from which they are obtained. The following are those principally employed by dyers and tanners: Gambier catechu, Bengal or Acacia catechu, Bombay or Areca catechu, and Mangrove cutch.

Gambier catechu.—Gambier, yellow cutch, cubical cutch, cube gambier, or terra japonica, is obtained from the *Uncaria Gambier*, an extensive scandent bush which is met with, both wild and cultivated, in Malacca, Penang and Singapore. The catechu is isolated by extracting the leaves and twigs with hot water until the liquid becomes syrupy, the insoluble matter being removed from time to time by means of a strainer. On cooling, the pasty mass is cut into 1 in. cubes and dried on bamboo trays.

Gambier catechu is largely used for the production on cotton of the well-known "catechu brown," which is exceedingly fast to light, acid and alkaline solutions, and also to bleaching powder. To obtain this, cotton is steeped in a hot solution of catechu (1–2%) to which has been added about 6% of copper sulphate, calculated on the weight of catechu employed. The material is allowed to remain in the bath as it cools, and without washing is treated in a second bath with a warm or boiling solution of potassium bichromate (0·1–0·2%). The colour is apparently intensified by the formation of a basic copper chromate.

Wool may be dyed with catechu in a similar manner to cotton, whilst in silk dyeing catechu is largely used for weighting purposes.

Bengal or Acacia Catechu.—Bengal catechu is derived from the *Acacia Catechu*, a tree 15–20 ft. high, which is common in most parts of India and Burma. To isolate the catechu which is present in the red heartwood, the tree is cut down whilst it is most full of sap, and the internal portion is sawn into small sticks and extracted with boiling water. The liquid is concentrated over a fire, and then allowed to evaporate spontaneously in shallow dishes. The extract thus obtained comes into the market as *Pegu* catechu, brown cutch, and brown catechu (Crookes, "Dyeing and Calico Printing," Longmans, 1874).

A purer substance, *kath*, or the pale catechu of India, is prepared by suspending twigs in the hot concentrated extract and collecting the crystals which thus separate.

Bombay or Areca Catechu.—This variety is obtained from the fruit of the *Areca Catechu*, or betel-nut palm, a tree which is common in tropical Asia. It possesses a bright chocolate and sometimes an orange-brown colour, and yields, on dyeing, very similar results to the ordinary cutches.

Mangrove Cutch.—This is obtained from the bark of the mangrove *Ceriops Candolleana*, and is of somewhat recent employment. In its preparation it is preferable to extract the fresh bark, which is of a light colour internally, rather than the stored product which has become red, or is said to have "sweated." For many purposes, mangrove cutch is said to be competing closely with the other varieties of catechu.

Although catechu received perhaps greater attention than other natural dyes, the results were so varied that the chemistry of the subject was for a long time in a most unsatisfactory condition. Some confusion arose from the non-appreciation of the fact that the main constituents of Gambier and Acacia catechu are not identical, and some uncertainty also apparently existed as to the botanical origin of the commercial varieties.

CATECHIN.

Catechin, the crystalline principle of Gambier catechu, was first described by Nees van Esenbeck (Annalen, 1832, **1**, 243), was subsequently examined by Berzelius (Jahresber. 1837, **14**, 235), and more recently by numerous chemists.

It was shown by von Kostanecki and Tambor (Ber. 1902, 35, 1867) and simultaneously by Perkin and Yoshitake (J.C.S. 1902, 81, 1162) that its formula is correctly represented as $C_{15}H_{14}O_6,4H_2O$.

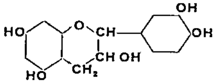
Catechin forms colourless needles, and when crystallised from water the air-dry product melts at 96° (Clauser, Ber. 1903, 36, 101); after standing over sulphuric acid, the water of crystallisation is lost, and the anhydrous substance melts at 176°–177°. Catechin is readily soluble in boiling water and cold alcohol, and gives with lead acetate solution a colourless precipitate, and with ferric chloride a deep green liquid. With pine wood and hydrochloric acid it gives the phloroglucinol reaction. On fusion with alkali, protocatechuic acid, phloroglucinol, and probably acetic acid are produced, and it is interesting to note that catechu has been considerably employed for the commercial preparation of protocatechuic acid.

From Bengal or Acacia catechu, Perkin and Yoshitake (*l.c.*) isolated *acacatechin*,

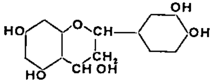
$$C_{15}H_{14}O_6,3H_2O,$$

which melts at 204°–205°, and is somewhat more sparingly soluble in water than catechin. When fused with alkali, acacatechin gives the same decomposition products as catechin. On the other hand, the melting points of the substances themselves and also of their derivatives differ widely, and it is thus evident that catechin and acacatechin are isomerides.

By oxidising an aqueous suspension of catechin tetramethyl ether with potassium permanganate, Perkin (J.C.S. 1905, 87, 398) obtained veratric acid and most probably phloroglucinol dimethyl ether, and as the result of his investigation considered that catechin was possibly a reduction product of quercetin and possessed either formula (I) or (II).



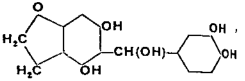
I.



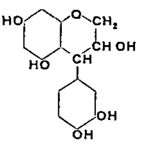
II.

It is interesting to note, in this connection, that a small quantity of quercetin is present in catechu (Löwe, Z. anal. Chem. 1874, 13, 113; Perkin, J.C.S. 1897, 71, 1135).

S. von Kostanecki and Lampe (Ber. 1906, 39, 4007; 1907, 40, 4910) concluded from their study of the subject that catechin is represented by formula (III), whilst Nierenstein (J.C.S. 1920, 117, 971, 1151; 1921, 119, 164) suggested formula (IV).

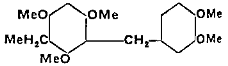


III.

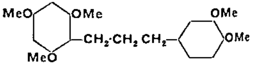


IV.

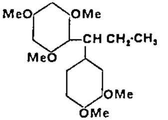
By the reduction of catechin tetramethyl ether, followed by methylation, von Kostanecki obtained a pentamethyl ether which he considered to be 2.4.6 trimethoxy-3 ethylphenyl 3′:4′-dimethoxyphenyl methane (V). On the basis of the formula (I or II) assigned to catechin by Perkin, this reduction and methylation product should be the pentamethoxy αγ-diphenylpropane derivative (VI), whilst according to Nierenstein's formula (IV) the product should be the αα-diphenylpropane derivative (VII). Freudenberg (Ber. 1920, 53, [B], 1416)



V.



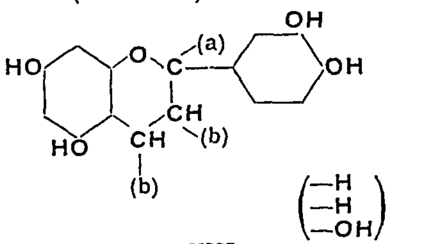
VI.



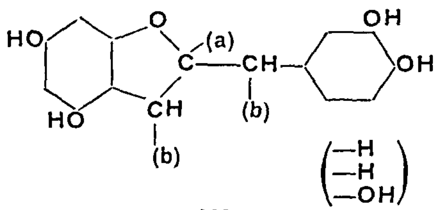
VII.

settled this point by the synthesis of 2.4.6.3′:4′-pentamethoxy-αγ-diphenylpropane (VI). The condensation of phloracetophenone trimethyl ether with veratraldehyde yields 2.4.6 trimethoxyphenyl 3′:4′-dimethoxystyryl ketone, from which, by reduction with hydrogen in presence of platinum, 2.4.6.3′.4′ pentamethoxy-

αγ-diphenylpropane (VI) is obtained. The identity of this substance with von Kostanecki and Lampe's methylated reduction product of catechin tetramethyl ether, and also with the corresponding product from acacatechin tetramethyl ether, was conclusively established by Freudenberg (*l.c.*; Z. angew. Chem. 1921, 34, 247) and Freudenberg, Böhme, and Beckendorf (Ber. 1921, 54, [B], 1204), and it was evident that formulæ (III) and (IV) must be abandoned in favour of formula (VIII) or an alternative structure (formula IX).



VIII.



IX.

Catechin and acacatechin yield acetyl and benzoyl derivatives which are optically active, indicating that the free compounds are optical isomerides, the former being *d*-catechin and the latter a mixture of *l*-catechin and *dl*-catechin (Freudenberg, Böhme, and Beckendorf, *l.c.*). Thus, acetyl Gambier catechin has $[\alpha]_D^{17}$ +40·6° in *s*-tetrachloroethane, whereas acetylacacatechin is lævorotatory, and from this a racemic compound, m.p. 165°, can be isolated by repeated crystallisation. When the crude lævorotatory acetyl derivative from acacatechin is mixed with the calculated amount of the penta-acetyl compound derived from Gambier catechin, the *r*-derivative is obtained in theoretical amount. Similarly, when pentabenzoylacacatechin is mixed with the requisite quantity of pentabenzoyl Gambier catechin, pentabenzoyl-*r*-catechin, m.p. 185°, is obtained.

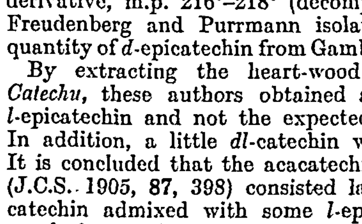
As a result, Freudenberg, Böhme, and Purrmann (Ber. 1922, 55, [B], 1734) conclude that the fifth hydroxyl group in catechin occupies a position marked (*a*) or (*b*) in formula (VIII) or (IX). If this hydroxyl is attached to the carbon atom (*a*), one asymmetric carbon atom only is present, and catechin thus will only exist in two active and a racemic form. If, however, the hydroxyl is attached at either of the two positions marked (*b*), two asymmetric carbon atoms must be present in this substance, pointing to the existence of two racemic and four active forms. The latter must be the case, for on boiling *r*-catechin in sodium chloride solution a partial transformation into *r*-*epicatechin* occurs. This conclusion is confirmed by Freudenberg and Purrmann (Ber. 1923, 56, [B], 1185), who describe in detail the separation of *l*- and *r*-catechins and *l*- and *r*-epicatechins from *Acacia Catechu*, the compounds being obtained in the relative amounts 60:320:30:30. Two specimens of *Acacia Catechu* from India consisted (i) of nearly homogeneous *r*-catechin and (ii) of a mixture of approximately equal amounts of *r*- and *l*-catechins. Further, it is shown that *d*-catechin in aqueous solution at 125° passes into *r*-catechin and *r*- and *d*-epicatechins. *d*-Epicatechin was isolated in the homogeneous state, and it was thus possible to place beyond doubt the racemic nature of *r*-epicatechin.

According to Nierenstein (Ber. 1923, 56, [B], 1877), tetramethylacacatechin can be converted into a pentamethyl derivative identical with the pentamethyl derivative of "catechin-C" (Perkin and Yoshitake, *l.c.*). This, which occurs in small amount in cube Gambier and in Pegu catechu, is designated *isoacacatechin.* On the other hand, Freudenberg and Purrmann (Annalen, 1924, 437, 274) observe that "catechin-C" [m.p. 235°–237°, disazobenzene derivative, m.p. 215°–217° (decomp.)] is identical with *d*-epicatechin, m.p. 245° (decomp.) [disazobenzene derivative, m.p. 216°–218° (decomp.)]. Again, Freudenberg and Purrmann isolated a small quantity of *d*-epicatechin from Gambier catechu.

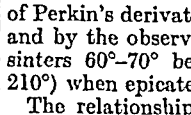
By extracting the heart-wood of *Acacia Catechu*, these authors obtained almost pure *l*-epicatechin and not the expected *l*-catechin. In addition, a little *dl*-catechin was isolated. It is concluded that the acacatechin of Perkin (J.C.S. 1905, 87, 398) consisted largely of *dl*-catechin admixed with some *l*-epicatechin, a conclusion confirmed by mixed melting-points of Perkin's derivatives with those of *dl*-catechin, and by the observation that *dl*-catechin always sinters 60°–70° below its melting-point (205°–210°) when epicatechin is present.

The relationships of the catechins as determined by experiment are shown in Table I (p. 436), whilst Table II (page 436) gives the properties of the various isomerides and their derivatives.

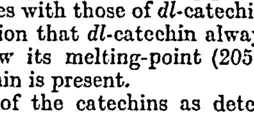
Freudenberg, Orthner, and Fikentscher (Annalen, 1924, 436, 286) show that four formulæ are possible for catechin, viz :



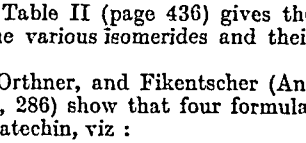
X.



XI.



XII.



XIII.

TABLE I.

(M = mixture, T = transformation, R = racemisation.)

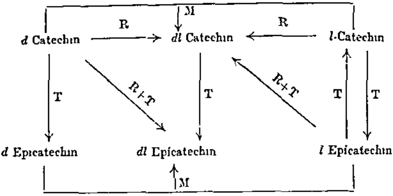
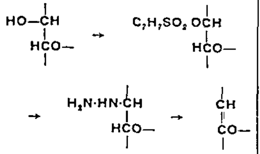


TABLE II

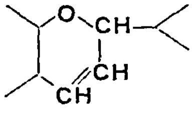
	Catechin			Epicatechin		
	d	*l*	*dl*	*d*	*l*	*dl*
Crystalline form .	Slender needles	Slender needles	Slender needles	Thick prisms	Thick prisms	Thick prisms also needles
Melting point . .	$+4H_2O$, 93°–95°, anhydr 174°–175°	$+4H_2O$, 93°–95°, anhydr 174°–175°	212°–214°	245°	245°	224°–226°
Water of crystallisation	0 or $4H_2O$	0 or $4H_2O$	$3H_2O$	$4H_2O$	$4H_2O$	Prisms, $4H_2O$ Needles, $1H_2O$
$[\alpha]_{578}$ in alcohol .	$[\alpha]_{546}^{\pm 0} = -2$	$[\alpha]_{546}^{\pm 0} = -2$	—	+68 9° (7%)	−68 2° (6%)	—
,, in aqueous acetone	+17 1° (9%)	+16 8° (3%)	—	+59 9° (4%)	−59 0° (4%)	—
Penta acetyl . m.p.	131°–132°	131°–132°	164°–165°	151°–152°	151°–152°	169°
$[\alpha]_{578}$ . .	+40 6° (3%)	−40 3° (2%)	—	+15 5° (3%)	−14 9° (2%)	—
Tetramethyl- . m p	143°–144°	143°–144°	142°	153°–154°	153°–154°	141°–142°
$[\alpha]_{578}$. . . .	−13 4° (3%)	+13 9° (3%)	—	+61 5° (2%)	−61 5° (4%)	—
Pentamethyl- m.p	90°–91°	90°–91°	110°–111°	—	93°–94°	—
$[\alpha]_{578}$. . .	+8 3° (1%)	+7 9° (5%)	—	—	−93 8° (2%) $[\alpha]_{546}$ = −106 5° (2%)	—
Tetramethylacetyl m.p	95°–96°	95°–96°	134°–135°	91°–92°	91°–92°	160°–161°
$[\alpha]_{578}$ . .	+6 8° (10%)	−6 6° (3%)	—	+71 6° (7%)	−71 2° (5%)	—
Tetramethyl toluene-sulphonyl m p	86°–87°	86°–87°	156°–157°	—	—	—
$[\alpha]_{578}$ . .	+22 7° (9%)	−22 7° (8%)	—	—	—	—
Pentabenzoyl- . m p	167°–169°	167°–169°	181°–182°	Not crystallised.		—
$[\alpha]_{578}$ . . .	+56 7° (6%)	−56 3° (5%)	—			

For deciding between these formulæ, reactions which had been serviceable for the determination of the structure of diacetone glucose were employed. Thus the toluenesulphonyl derivative is boiled with hydrazine, when the following changes occur—

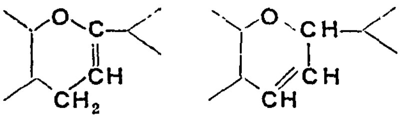


with elimination of the original hydroxyl group and adjacent hydrogen atom. The toluene sulphonic ester of tetramethyl-*d*-catechin, thus treated, yielded phloroglucinol dimethyl ether and *3-m p-dimethoxyphenylpyrazoline*, together with a small amount of the primary hydrazine. Hence a *trans* configuration of the hydroxyl group in *d*-catechin tetramethyl ether is indicated. It was subsequently found by Freudenberg, Fikentscher, and Harder (Annalen, 1925, 441, 157) that *l* epicatechin tetramethyl ether behaves as the *cis*-isomeride, since its *p* toluenesulphonyl derivative reacts with hydrazine yielding the unsaturated compound *anhydro-epicatechin tetramethyl ether*, m p. 119°, in 70% yield.

Formula (XIII) must be discarded since *cis trans* isomerism is not possible unless the hydroxyl group is in the hydrogenated ring system. Formulæ (X), (XI), and (XII) permit of the production of the respective anhydro-derivatives (*a*), (*b*, 1 and 2), and (*c*) :

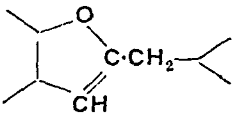


(a)



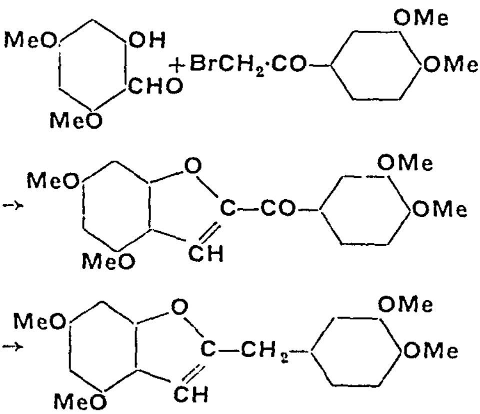
(1) (2)

(b)

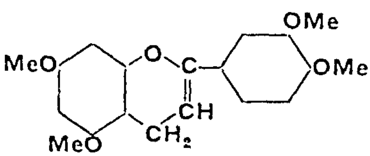


(c)

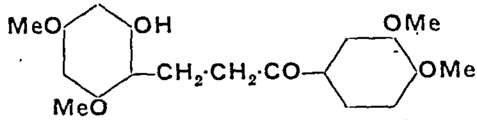
Freudenberg, Fikentscher, and Wenner (Annalen, 1925, 442, 309) settled this question by the synthesis of (c). Phloroglucinaldehyde dimethyl ether condensed with ω-bromoacetoveratrone yields 4:6-dimethoxy-2-(3′:4′-dimethoxybenzoyl)coumarone, and from this, by reduction with sodium and amyl alcohol, 4:6-dimethoxy-2-(3′:4′-dimethoxybenzyl)coumarone (c), is obtained:



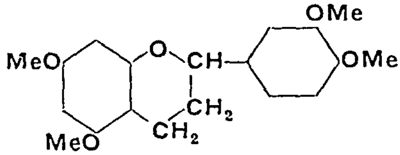
As this substance is not identical with tetramethylanhydroepicatechin, the latter must, therefore, have the structure :



Consequently (XII) is untenable for catechin, which thus has the constitution (XI). This is supported by the fact that tetramethylanhydroepicatechin in moist acetic acid solution passes into 3′:4′-dimethoxyphenyl β-2-hydroxy-4:6-dimethoxyphenylethyl ketone :



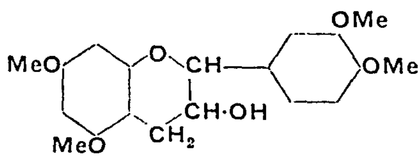
identical with the product obtained by hydrogenating 3′:4′-dimethoxyphenyl β-2-hydroxy-4:6-dimethoxystyryl ketone (*cf.* Pratt, Robinson and Williams, J.C.S. 1924, 125, 206). Further, synthetic 3′:4′-dimethoxyphenyl β-2-hydroxy-4:6-dimethoxyphenylethyl ketone and tetramethylanhydroepicatechin give with hydrogen chloride the same *hydrochloride*, which, on hydrogenation, yields 5:7:3′:4′-tetramethoxyflavan :



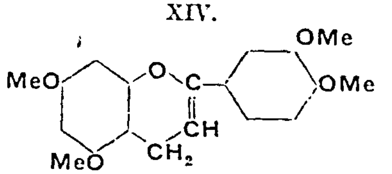
identical with tetramethyldeoxyepicatechin, a compound earlier prepared by Freudenberg, Fikentscher, and Harder (*l.c.*) from anhydroepicatechin tetramethyl ether.

In final confirmation of the structure assigned to catechin, Freudenberg, Fikentscher, Harder, and Schmidt (Annalen, 1925, 444, 135) obtained *dl*-epicatechin and pentamethyl-*dl*-epicatechin by catalytic reduction of cyanidin chloride and its pentamethyl ether, respectively. In a similar manner, Freudenberg and Kammüller (Annalen, 1927, 451, 209) prepared *dl*-epicatechin pentamethyl ether from quercetin pentamethyl ether, whereas deoxyepicatechin tetramethyl ether was thus produced from luteolin tetramethyl ether.

Whereas tetramethylepicatechin (XIV, containing the H and OH groups in the *cis*-position) on dehydration yields the tetramethoxyflavene (XV) (*l.c.*), Freudenberg, Carrara, and Cohn (Annalen, 1925, 446, 87), by dehydration of tetramethylcatechin (XIV, in which the H and OH groups are in the *trans*- position), obtained the substance (XVI), the production of which arises from the migration of the dimethoxyphenyl group during dehydration. This substance had in reality previously been



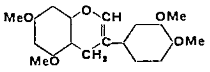
XIV.



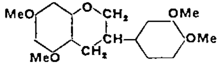
XV.

obtained by Drumm (Proc. Roy. Irish Acad. 1923, 36, 41 ; *see also ibid.* 1924, 36, [B], 149 ; 1929, 39, [B], 114) by the action of phosphorus

pentachloride on tetramethylcatechin and treatment of the product with pyridine. By hydrogeneration (XVI) yields the chromane derivative (XVII), the constitution of which was proved by synthesis (Freudenberg, Carrara, and Cohn, *l.c.*)

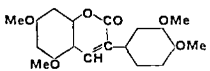


XVI.



XVII.

Baker (J.C.S. 1929, 1593), by the oxidation of anhydrocatechin tetramethyl ether, obtained 5:7:3′:4′-tetramethoxy-3 phenylcoumarin :



and a *substance* which with boiling hydrochloric acid gives 5.7:3′.4′-tetramethoxy*iso*flavylium chloride. The following compounds were shown to be identical: 5.7.3′:4′ tetramethoxy*iso*flavylium chloride with the "hydrochloride" of anhydrocatechin tetramethyl ether (Freudenberg, Carrara, and Cohn, *l c.*); the corresponding *iso*flavylium bromide with the bromide described by Drumm (*l c.*); and the "hydrochloride" of anhydroepicatechin tetramethyl ether with tetramethylluteolinidin chloride (Pratt, Robinson, and Williams, *l c*).

Catechutannic Acid.—In addition to catechin, Gambier catechu contains a small amount of catechutannic acid, and this substance is present in considerable quantity in the browner varieties of cutch. It consists of an amorphous reddish-brown powder, readily soluble in water and alcohol, insoluble in ether. Catechutannic acid gives a precipitate with lead acetate solution and also resembles catechin in giving a green coloration with ferric chloride, and the phloroglucinol reaction with pinewood and hydrochloric acid. It is a powerful tanning agent, and appears to differ but little from the so-called "catechol" tannins.

Catechutannic acid is said to be an anhydride of catechin and to be produced when an aqueous solution of catechin is heated to 110°, or by boiling catechin with solutions of the alkali carbonates.

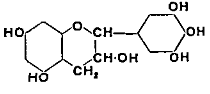
Finally, there are present in catechu certain brown substances known as *rubinic* and *japonic acids* which, according to some writers, appear to have been formed by the oxidation of the catechin. Their chemical nature is, however, unknown.

Catechin, though largely employed for tanning purposes, does not precipitate a gelatin solution, and is not itself a tannin matter. On the other hand, it is adsorbed by the hide, and there passes gradually into catechutannic acid.

Details for the extraction and valuation of Gambier are given by Eaton and Bishop (J. Soc. Leather Trades' Chem. 1926, **10**, 395) Hooper (Analyst, 1925, **50**, 162) describes a method for differentiating the proportions of tannin and catechin in commercial samples of cutch and Gambier.

According to Freudenberg, Böhme and Purrmann (*l.c.*), the catechin from Chinese rhubarb is pure *d*-catechin; that from steamed mahogany contains *dl*- and *d*-catechin, and probably also *d* epicatechin. The catechin from *Paullinia Cupana* is similar to that from mahogany.

From green tea, Tsujimura (Sci. Papers Inst Phys. Chem. Res. Tokyo, 1929, **10**, 252; 1934, **24**, 149) isolated a catechin, evidently *l* epicatechin in the anhydrous form, and *tea catechin II*, or *gallocatechin*, m p. 218°, $[\alpha]_D^{18°}$ −67 5°, to which the formula



is assigned. The *pentamethyl ether* melts at 183°. By extracting fresh Formosan tea leaves with water, Oshima (Bull. Agric. Chem. Soc. Japan, 1936, **12**, 103; Proc. Imp. Acad. Tokyo, 1936, **12**, 189) obtained *l* epicatechin, gallic acid, an amorphous *tannin*, $C_{30}H_{24}O_{14}$, and a *gallocatechin*, $C_{15}H_{14}O_7$, m p. 227°, $[\alpha]_D$ −37 5° in water, −67·0° in alcohol (*penta-acetate*, m p. 189°, *pentamethyl ether*, m.p. 184°), evidently identical with that isolated by Tsujimura. The amorphous tannin and the gallocatechin were shown by synthesis to be *bis*-(5:7:3′:4′·5′-*pentahydroxy*)-*flavpinacol*, and 3:5.7 3′.4′:5′-*hexahydroxyflavan* respectively.

Freudenberg and Oehler (Annalen, 1930, **483**, 140) isolated *d*-catechin and *l* epicatechin as sole products from fresh kola nuts, and thus the names kolatin, kolatein (Goris, Compt. rend. 1907, **144**, 1162), and cola-catechin (Casparis, Pharm. Acta Helv. 1929, **4**, 181, 189) should be deleted from the literature. Contrary to the statement of Casparis (*l c.*), no catechin is present in fresh or dry tormentilla root.

d-Catechin is present in the fruit of *Areca Catechu*, L. (Yamamoto and Muraoka, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **19**, 142) and in the bark of the peach tree (Collot and Rabaté, Compt. rend. 1936, **202**, 1208).

Freudenberg, Cox and Braun (J. Amer Chem. Soc. 1932, **54**, 1913) show that *l*-epicatechin is present in the cacao bean (*cf.* Adam *et al.*, *ibid.* 1931, **53**, 727).

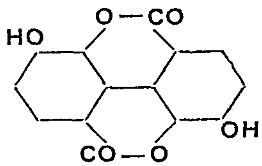
From "rhatany root" from Bolivia (*Krameria argentea* Mart.), Nierenstein (J.C.S. 1932, 2809) isolated *d*- and *dl*-gambir-catechin. These two catechins are also present in the cutches from the leaves of *Uncaria Gambier* Roxb, and *U. acida* Roxb. (*Nierenstein and co-workers*, J. Amer. Chem. Soc., 1931, **53**, 1505).

A. G. P. and E. J. C.

CATECHUTANNIC ACID *v.* CATECHU OR CUTCH.

CATELLAGIC ACID. Schiff (Ber. 1882, 15, 2590) obtained this acid by heating protocatechuic acid with arsenic acid, and assigned the formula $C_{14}H_{10}O_7$ or $C_{14}H_8O_7$. Perkin and Nierenstein (J.C.S. 1905, 87, 1417) obtained apparently the same substance by the oxidation of protocatechuic acid or *p*-hydroxybenzoic acid with potassium persulphate and sulphuric acid. Catellagic acid crystallises from pyridine in colourless needles which melt above 300° and sublime with but moderate carbonisation at higher temperatures. Solutions of the alkali hydroxides dissolve it with a pale yellow colour, and with nitric acid it gives a magenta-coloured liquid. By distillation with zinc dust fluorene is obtained.

Catellagic acid is closely related to ellagic acid and has the following constitution :



Diacetylcatellagic acid, colourless prismatic needles, melts at 322°–324°.

A. G. P. and E. J. C.

CATHARTIN, CATHARTOGENIC ACID. An infusion of the leaves and pods of the Alexandrian shrub *Cassia acutifolia.* It is used as a cathartic.

CATHIDINE, CATHININE *v.* CATHINE.

CATHINE. *Catha edulis,* syn. *Celastrus edulis* (Fam. Celastraceæ) is a plant, the leaves of which are chewed as stimulant to a very large extent in Abyssinia and Yemen. The plant is indigenous to Africa, Turkestan, and Afghanistan (Owen, J.S.C.I. 1910, 29, 1091). For early literature and botanical investigation, *see* Beitter (Arch. Pharm. 1901, 239, 17) and Chevalier (Bull. Sci. Pharmacol. 1911, 18, 264). Stockman (Pharm. J. 1912, 35, 676) isolated three different alkaloids from *C. edulis* : *cathine* (cryst., yield 0·27%), *cathidine* (amorphous, 0·32%), and *cathinine* (cryst. (?), 0·15%) ; benzene seems to be the most suitable solvent for extraction.

Cathine, $C_9H_{13}ON$, m.p. 77° (from benzene), $[\alpha]_D^{20}$ +42·5° has been identified by Wolfes (Arch. Pharm. 1930, 268, 81) with d-*noriso-ephedrine,* the same compound which had been isolated from a Chinese ephedra (*cf.* Smith, J.C.S. 1928, 51 ; Nagai and Kanao, Amer. Chem. Abstr. 1929, 23, 1472). There is nothing known about the constitution of the two other alkaloids.

Schl.

CAULIFLOWER *v.* CABBAGE.

CAULOPHYLLINE, $C_{12}H_{16}ON_2$, occurs in *Caulophyllum thalictroides* (Linn.). It is methylcytisine.

CAUSTIC OIL OF ARSENIC *v.* ARSENIC, ARSENIC CHLORIDE.

CÂY CÂY FAT, or Cochin China wax, is obtained from the fruit of the Cây Cây tree, *Irvingia Oliveri* Pierre. The wax has the consistency and texture of beeswax, but is more brittle, m.p. 39·7°, d_{40}^{40} 0·913, acid value 0·86, saponification value 235·3, iodine value 6·7, Reichert-Meissl value 0·62, unsaponifiable value 0·42%. The wax is composed mainly of myristin 60–65%, laurin 30–35%, and olein about 5%.

CAYENNE PEPPER *v.* CAPSICUM.

CEDARITE *v.* AMBER.

CEDARWOOD CAMPHOR *v.* CEDROL.

CEDARWOOD, ESSENTIAL OIL OF. The oil distilled from the wood of various species of *Juniperus,* chiefly *J. virginiana* (Fam. Coniferæ) a tree found in North America. The wood is also imported from Honduras, Mexico, Trinidad, and Demerara. Yield 2–4%. The oil is a by-product from the manufacture of pencils.

Constituents.—The main constituent is the sesquiterpene cedrene. Cedrol or *cedar camphor,* a sesquiterpene alcohol, is present in variable quantity and separates from some oils in crystals which after crystallisation melt at 86°–87°. Two other sesquiterpene alcohols, cedrenol and pseduocedrol, have also been isolated.

Characters.—Sp.gr. at 15·5° 0·940–0·960, α_D^{20} −25° to −45°, n_D^{20} 1·495–1·510. It is used for microscopic purposes owing to its high refractive index. A specially prepared oil containing other substances has a refractive index of 1·515–1·526.

C. T. B.

CEDRA-CEDRAT (Fr. *Cédrat*). The fruit of the citrus, *Citrus medica* (Fam. Rutaceæ). The peel is very thick, covered with an epidermis containing a fragrant essential oil, used for flavouring preserves, also used whole for wet comfits, and cut in quarters for dry comfits. A liqueur is made from it by gathering the fruit before it is ripe and grating the peel into brandy.

CEDRELA TOONA. The *Cedrela Toona,* the Toon or Indian mahogany tree, is a large tree 50–60 ft., although occasionally reaching 100 ft., in height, the wood of which closely resembles mahogany and is imported into England under the name of " Moulmein Cedar," and much used for making furniture. It occurs in the tropical Himalaya from the Indus eastward, throughout the hilly districts of Central and Southern India to Burma, and is also found in Java and Australia. The flowers constitute one of the less important Indian natural dyestuffs, and are reputed to yield both a red and a yellow dye (known in Bengal as " Gunari," which is applied without mordants). The seeds are also stated to give a red dye. Although employed for dyeing purposes alone, the flowers are also used in Burma in conjunction with safflower, and together with turmeric to produce the sulphur-yellow colour or " basanti " of Cawnpore.

Perkin (J.C.S. 1912, 101, 1538) examined the flowers of the *Cedrela Toona* and isolated a colouring matter which crystallised from pyridine in orange leaflets ; these contained pyridine and became red and opaque when washed with benzene or alcohol, the pyridine being thus eliminated. The substance melted at 285°–287° and proved to be identical with the red colouring matter *nyctanthin* isolated by Hill and Sirkar (J.C.S. 1907, 91, 1501) from the

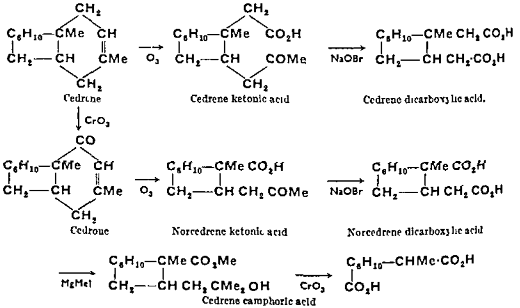
flowers of the *Nyctanthes Arbor tristis.* The amount which is present in the Toon flowers is very small and does not seem to average more than 0.1%. The general similarity of the properties of nyctanthin to those assigned to bixin (*v.* ANNATTO, BIXIN) led Perkin to conclude that the two compounds are closely related. This conclusion was confirmed by Kuhn and Winterstein (Helv. Chim. Acta, 1929, 12, 496), who showed that nyctanthin is identical with crocetin, the colouring matter of saffron (*v.* CAROTENOIDS).

The flowers of the *Cedrela Toona* contain in addition to crocetin a fair amount of quercetin, probably as glycoside, and also a second flavone or flavonol dyestuff the identity of which was not ascertained. A sugar, $C_{12}H_{22}O_{11}$, m.p. 165°–168°, is also present.

Dyeing Properties.—Cotton and woollen fabrics can be dyed a dull yellow colour by mere immersion in a boiling extract of Toon flowers. *This, however, is not permanent, and is removed,* although much more quickly from cotton than wool, by the action of soap or dilute alkali. Better results are obtained by the employment of mordants, and the following shades are obtained with mordanted woollen cloth: dull brownish-yellow (chromium), full golden-yellow (aluminium), bright yellow (tin), and dull olive-brown (iron). During these operations, crocetin or its glycoside apparently plays no part, and the colours obtained are due to the flavone glycosides present. A. G. P. and E. J. C.

CEDRENE. The sesquiterpene hydrocarbon *cedrene*, $C_{15}H_{24}$, b.p. 121°/12 mm., d_4^{17} 0.9367, n_D^{17} 1.5030, α_D −52.8°, occurs in cedar wood oil (from *Juniperus virginiana*) and was first isolated from this oil by Walter (Annalen, 1841, 39, 247; 1843, 48, 35). It can be obtained also by the dehydration of the alcohol *cedrol* (*q.v.*). Cedrene is probably most conveniently identified by its oxidation with chromic acid to the ketone *cedrone*, $C_{15}H_{22}O$, m.p. 32°–33°, d^{15} 1.014, n_D^{23} 1.51293, $[\alpha]_D$ −91.4°, *semicarbazone*, m.p. 242°–243°. This ketone was prepared first by Rousset (Bull. Soc. chim. 1897, [iii], 17, 485) and it has since been studied by Semmler and Hoffmann (Ber. 1907, 40, 3525), Ruzicka and van Melsen (Annalen, 1929, 471, 54), and by Blumann, Hellriegel and Schulz (Ber. 1929, 62, [B], 1698; 1931, 64, [B], 1540). The last mentioned authors showed that cedrene on auto-oxidation in the presence of cobalt resinate gave a *secondary alcohol*, $C_{15}H_{24}O$, m.p. 103.5°, b.p. 160°/12 mm., $[\alpha]_D$ −217° (in alcohol), from which cedrone could be obtained by oxidation with chromic acid.

The oxidative degradation of cedrene and of cedrone has been investigated by Semmler and his collaborators (Ber. 1907, 48, 3523; 1912, 45, 355, 791, 1389, 1556) and by Ruzicka and van Melsen (Annalen, 1929, 471, 54). According to Ruzicka and van Melsen the reactions which occur are best explained in accordance with the scheme given below:



More recently Treibs (Ber. 1935, 68, [B], 1041) has observed that cedrene yields *p*-cymene when it is heated with a nickel pumice catalyst at 420°–450°, whilst by oxidation he has separated an acid, which he suggests is camphoronic acid. The bearing of these results on the structure of cedrene has been discussed by Short (J.S.C.I. 1935, 874), Robinson and Walker (*ibid.* 906, 946), and by Ruzicka and Jutassy (Helv. Chim. Acta, 1936, 19, 322).

On catalytic hydrogenation cedrene yields *dihydrocedrene*, b.p. 122°–123°/10 mm., d^{20} 0.9204, n_D^{20} 1.4929, $[\alpha]_D^{20}$ +2°. J. L. S.

CEDRIRET. A substance found in wood tar by Reichenbach and recognised by Liebermann as a quinone like substance and termed by him *coerulignone*. Hofmann showed that it was tetramethoxydiphenyl quinone, formed by the oxidation of pyrogallol dimethyl ether.

CEDROL. The sesquiterpene alcohol, *cedrol*, $C_{15}H_{26}O$, m.p. 86°, b.p. 292°, known also as *cedar camphor* and *cypress camphor*, occurs in cedarwood oil (from *Juniperus virginiana*), in cypress oil (from *Cupressus sempervirens*) and in the oils from *J. chinensis* and *Origanum smyrnæum*. Cedrol is, as a rule, dextrorotatory ($[\alpha]_D$ +10·5° in the chloroform), but in a number of cases it has been found to be optically inactive. The alcohol was first isolated by Walter (Annalen, 1841, **39**, 247; 1843, **48**, 35) and later studied by Gerhardt (Traité, 1856, IV, 353), and by Rousset (Bull. Soc. chim. 1897, [iii], **17**, 485), who suggested that it was a tertiary alcohol and prepared an *acetate*, b.p. 157°–168°/8 mm. It was shown by Semmler and Spornitz (Ber. 1912, **45**, 1553) that it can be readily dehydrated by digestion with formic acid to give the tricyclic hydrocarbon, *cedrene* (*q.v.*). Cedrol has been characterised by the preparation of a *phenylurethane*, m.p. 106°–107°. It has been found by Semmler and Spornitz (Ber. 1912, **45**, 1384) that cedarwood oil does not always contain crystalline cedrol, but that the sesquiterpene alcohol present is a *ψ-cedrol*, b.p. 147°–152°/9 mm., d^{20} 0·9964, n_D^{20} 1·5131, $[\alpha]_D$ +21·5. Like cedrol, *ψ*-cedrol yields cedrene on dehydration, and it is converted into the crystalline alcohol by digestion with potassium or when its xanthate is hydrolysed (Kimura, Ber. deut. pharm. Gess. 1910, **20**, 293). It is probable, therefore, that the two alcohols are stereoisomerides. According to Bell (J.C.S. 1930, 1908) *ψ*-cedrol is obtained when cedrene is oxidised with mercuric acetate.

J. L. S.

CELASTOID *v.* CELLULOSE PLASTICS.

CELERY, CELERIAC. Common edible celery consists of the blanched stems of *Apium graveolens* Linn. Turnip-rooted celery or celeriac is a variety (var. *rapaceum* Mill.) in which the upper part of the root is much enlarged. The bulbous root is boiled and eaten as a vegetable. The following are typical analyses of celery:

	H_2O	Protein.	Fat.	N-free extract.	Fibre.	Ash.
German[1]	90·5	1·34	0·27	5·87	1·01	0·97
American[2]	94·5	1·1	0·1	3·3		1·0

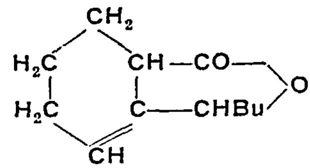
[1] von Schleinitz (Landw. Jahrb., 1918, 52, 131).
[2] Atwater and Bryant (U.S. Dept. Agric. Off. Exp. Sta. Bull. 1906, No. 28).

Coons and Klotz (J. Agric. Res. 1925, **31**, 287) give the nitrogen distribution of healthy celery stalks as: ammoniacal N 0·3, nitrate N 5·8, hydrolysable N 88·8, acid amide N 13·5, humin N 9·6, total amino N 47·1, protein N 67·8, non-protein N 32·1%. Asparagine and tyrosine are among the nitrogenous constituents.

Mannitol is generally distributed throughout the plant, and among carbohydrate constituents there are small amounts of sucrose and reducing sugars (Obaton, Compt. rend. 1929, **188**, 77). Celery also contains approximately 1·5% of pentosans, a glucoside apiin, and inosite.

Stems of petioles of celery contain specialised cells in which an oleoresin and an essential oil accumulate. The discoloration of celeriac occurring frequently on boiling is attributed to enzymic resinification of the oil effected by atmospheric oxygen (Schuphan, Bodenk. Pflanzenernähr. 1937, **2**, 255–304). The oil has the characteristics, d^{15} 0·866–0·894, $[\alpha]_D$ +60° to +82°, acid value 4, ester value 16–45, n_D^{20} 1·486, terpenes 70% (60% limonene and 10% *d*-selinene). According to the Établissements Antoine Chiris (Parfums de France, 1936, **14**, 12) the essential oil occurring in celery seed differs considerably from that of stalks and leaves and is characterised by d^{15} 0·9165, $[\alpha]_D$ +55° 45′, acid value 1·12, ester value 74·9.

The characteristic odour and flavour of celery and celeriac is ascribed to the presence in the essential oil of the anhydride of sedanonic acid, $CO_2H{\cdot}C_6H_8{\cdot}CO{\cdot}C_4H_9$, and the lactone of sedanolic acid, sedanolide (Ciamician and Silber, Ber. 1897, **30**, 1419):



Palmitic acid and a phenolic substance are also present in the oil.

Celery ash has the following composition as percentage of total ash:

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.
Shoots	33·1	19·3	13·1	—	—
Root	43·2	—	13·1	5·8	1·4

	P_2O_5.	SO_3.	SiO_2.	Cl.	CO_2.
Shoots	14·4	1·2	1·9	22·1	10·9
Root	12·8	5·6	3·8	15·9	—

Various records of the minor elements in celery include Fe 3·5–8·0, Mn 1·1, Cu 0·1–1·2 mg. per kg. (fresh basis), and in celeriac Mn 7·5, Cu 6·6, Zn 2·1 mg. per kg.

A. G. Po.

CELERY, ESSENTIAL OIL OF *v.* CELERY.

CELERY SEEDS. The dried ripe fruits of *Apium graveolens* Linn. (Fam. Umbelliferæ), a native of the temperature regions of Europe, but cultivated extensively. For official medicinal purposes, the fruit must be collected from cultivated plants, which are too well known to require description. The wild plant grows in marshy places and has a disagreeable taste and odour, which are not present in the cultivated variety. The fruits consist of a cremocarp, composed of two mericarps, which may be united or separate. The cremocarps are about 0·8–1·5 mm. long, 1 mm. broad, and 0·5 mm. thick. Celery seed is commonly employed as a flavouring material, particularly in celery salt, from which it should be separated for examination by its insolubility in water. It is also used

as a sedative and is popularly believed to be effective as a cure for rheumatism. The cultivated stalks, leaves and roots are employed to a large extent as a salad or vegetable, and when dried in soup powders.

Microscopic Appearance.—The cross-section of the mericarps is almost that of an equilateral pentagon, and there are 6–15 vittæ, or oil cells, in the mesocarp, 1, 2, or 3 in each groove of the dorsal side, but 2 only on the commisural side. The epidermal cells are polygonal with wavy walls and the cuticle is thick and tough, though delicately striated. The endocarp and seed are such as are usually found in other seeds of the Umbelliferæ.

Chemical Composition.—The principal constituent is the essential oil, and this is probably determined most satisfactorily by the method of Cocking and Middleton (Quart. J. Pharm. 1935, 8, 435). The seed is mixed with brine and distilled, the vapours being passed through the top of a condenser into a graduated tube, in which the oil is collected whilst the condensed water is returned to the distillation flask. An air inlet or outlet is provided by means of a side tube below the condenser and above the graduated tube. The seed contains about 1 83% of volatile oil, for further details of which *see* CELERY.

Standards.—The "British Pharmaceutical Codex" suggests that the fruits should not contain more than 4% of foreign seeds and 1% of other organic matter, and not more than 2% of ash insoluble in acid. The "National Formulary" suggests that the total ash should not exceed 8%.

Adulteration.—Mustard seed and other cheaper seeds are used to mix with celery seed, and the author has a sample containing henbane seeds as adulterant T. McL.

CELESTINE or CELESTITE. Native strontium sulphate ($SrSO_4$), forming orthorhombic crystals isomorphous with baryte ($BaSO_4$). The crystals are colourless or yellowish, but sometimes they show a pale tinge of sky-blue, and on this account the mineral receives its name. The mineral is often very like baryte in appearance, and it is also heavy (sp gr. 3 9 ; of baryte, 4 5) ; it is most readily distinguished by the colour that the powdered mineral moistened with hydrochloric acid imparts to the Bunsen flame. Numerous finely crystallised specimens have been found in the red marls of Triassic age in the neighbourhood of Bristol, and in the sulphur mines near Girgenti in Sicily. Deposits of celestine occur in beds of Cretaceous age over a wide area in Russian Turkestan ; and the mineral is found also in Baluchistan. The largest crystals, measuring a foot across, are from a cave in limestone on Strontian Island, Lake Erie, Ohio. Workable deposits are mined in Arizona and California. The mineral is dug in numerous shallow pits in Gloucestershire and Somersetshire, where in 1902 the production amounted to 32,000 tons valued at about £1 per ton ; but since then it has declined to less than 10,000 tons per annum. Most of this was formerly exported to Germany, where in the form of strontium hydroxide it was used in the refining of beet-sugar. It is also converted into strontium nitrate for making red fire in pyrotechny. For details respecting the British occurrences, *see* "Special Reports on the Mineral Resources of Great Britain," vol. iii (Mem. Geol. Survey), 1915, 2nd ed. 1918; "Strontium Minerals," Imperial Mineral Resources Bureau, London, 1923. L. J. S.

CELESTINE BLUE. An oxazine dyestuff.

CELLASTINE *v.* CELLULOSE PLASTICS

CELLIAMIN, $C_{21}H_{35}O_2N$, m p. 127°–131°, is an alkaloid occurring in the root of *Helleborus viridis*

CELLITON DYES *v.* ACETATE SILK DYES.

CELLOBIASE is a member of the β glucase or β-heteroglucosidase (Oppenheimer) class of enzymes, originally described as emulsin. How far the members of this group are specific is at present uncertain. It hydrolyses cellobiose in which the junction of the two glucose residues is $C_1\beta-C_4$. It may also hydrolyse gentiobiose in which the junction is $C_1\beta-C_6$, in which case it is the same as gentiobiase and amygdalase.

The optimal p_H is 4 9–5 3. As yet very little which is positive is known about these enzymes (*see* Grassmann, Annalen, 1933, 502, 20 ; 503, 167 ; Neuberg and Hofmann, Biochem. Z. 1932, 256, 450 ; 265, 462). E. F. A.

CELLOBIOSE, $C_{12}H_{22}O_{11}$=glucose-4-β-glucoside. M.p. 225°. The free sugar was first obtained by acetolysis of cellulose (filter paper) by Skraup (Monatsh. 1901, 22, 1011). The constitution was definitely established by Haworth and Hirst (J.C.S. 1921, 119, 193 ; 1927, 2809) and by Zemplén (Ber. 1926, 59, 1254; 1927, 60, 1555).

It is hydrolysed by emulsin but not attacked by invertase or maltase.

The β-form has $[\alpha]_D$ +16° increasing to +35° on mutarotation. The calculated rotation of the α form is +72°.

It forms the usual derivatives of a reducing sugar. The *a-octacetate* has m.p. 229° $[\alpha]_D$ +42°. The *β-octacetate* has m.p. 202°, $[\alpha]_D$ −14 5°.

It has been synthesised by Freudenberg and Nagai (Ber. 1933, 66, [B], 27).

Cellobiose has never been found naturally *per se* ; it is a product of acetolysis of lichenin and tunicin. Chief interest attaches to it as a component of cellulose to which it bears the same relation as does maltose to starch. The successive degradation of cellulose yields first dextrins and then smaller molecules consisting of cellobiose, cellotriose, cellotetrose, and a cellohexose. The cellotriose is identical with a product described by Bertrand under the name procellose (Compt. rend. 1923, 176, 1583). The cellodextrins range in molecular size from chains of 10 to chains of 30 β glucose units. E. F. A.

CELLOMOLD *v.* CELLULOSE PLASTICS.

CELLOPHANE (registered name of the British Cellophane Co.). Cellophan. A transparent film of regenerated cellulose, used as a wrapping material for foodstuffs, fruit, tobacco, etc., manufactured by forcing a viscose (cellulose xanthogenate) through a long fine slot into an acid bath. It has been used in the laboratory

for osmoses experiments and when herepathite is incorporated in the film, a substitute for a Nicol's prism is obtained. Cellophane swells when immersed in water, and a varnished waterproof variety is manufactured.

CELLOSOLVE. This solvent, which is widely used in lacquer formation, is the ethylene glycol monoethyl ether and was one of the earliest of the synthetic solvents manufactured in the States by the Carbide and Carbon Chemicals Corporation, U.S.P. 1644420, 1927. The method of manufacture generally of the glycol mono ethers consists in heating under pressure a mixture of an olefine oxide and an organic hydroxy compound, catalysts not being used. As a case in point a mixture of ethylene oxide with twice the theoretical amount of ethyl alcohol is pumped through a system in which the temperature is raised to 180°C. and the pressure to 30 atm. Alternatively the olefine oxides may be heated with alcohol under pressure in the presence of di-ethyl or di-methyl sulphate, for example, ethylene glycol monoethyl ether can be obtained in a 90% yield by heating ethylene oxide with ethyl alcohol at 100°C. under a pressure of 50 lb. per sq. in. with the addition of a small amount of diethyl sulphate.

In general the mono alkyl ethers of ethylene glycol are odourless and colourless liquids. They dissolve cellulose nitrate, cellulose acetate, resins, oils and gums. Cellosolve itself boils at 134°C., has a density of 0·9360, refractive index 1·4042. The acetate of this ether (cellosolve acetate, *i.e.* ethylene glycol monoethyl ether acetate) boils at 153°C., and is a good solvent for cellulose nitrate and a variety of gums. The use of cellosolve demands adequate ventilation.

Higher homologues have been put forward as solvents, *e.g.* the mono amyl, the mono phenyl and the mono benzyl.

For a detailed account of this and similar materials, "The Chemistry of Petroleum Derivatives" by Carleton Ellis (Chemical Catalog Co.) should be consulted. A. E. D.

CELLOTROPIN. Benzoyl derivative of hydroquinone glucose, $C_{12}H_{16}O_7$ (mono-benzoyl arbutin), a glucoside found in pear leaves. M.p. 184·5°. Formerly prescribed for pulmonary tuberculosis.

CELLULASE. An enzyme which hydrolyses cellulose.

CELLULOID. Celluloid is the name usually applied in Europe to the thermoplastic colloid made from nitrocellulose and camphor. In America the word is the registered name of the product of one Company.

Alexander Parkes, of Birmingham, the inventor of the cold vulcanising process for india-rubber, and of the Parkes process for desilverising lead, was the first to discover the valuable properties imparted to nitrocellulose by mixing it with camphor. He exhibited small articles made from this mixture before the Royal Society of Arts in 1865, under the name of "Parkesine." The name "xylonite," by which the material is usually known in the United Kingdom, was adopted by one of Parkes's associates, Daniel Spill. Other American names besides "Celluloid" are "Pyralin," "Viscoloid," and "Fiberloid." Early development work in Great Britain was not successful, but the Hyatt brothers in the United States put the industry on an industrial footing. It returned to this country in the late 'seventies and has been manufactured here ever since. The estimated world production of celluloid is 40,000 tons.

The manufacture of celluloid is conveniently divided into three stages :

(1) The preparation of nitrocellulose.
(2) Plastification of nitrocellulose with camphor and shaping into sheets, tubes, and rods.
(3) The finishing processes applied to raw celluloid.

(1) Preparation of Nitrocellulose.—Nitrocellulose for the manufacture of celluloid is made almost entirely from cotton linters or purified wood cellulose. Linters is preferred when the best colour is required in the product. The percentage of nitrogen considered best for celluloid manufacture is from 10·7 to 11·1, which requires the use of a nitrating bath containing from 58–60% of sulphuric acid, and 20–23% of nitric acid. Different factories have their own standards, to which they adhere very closely. A patented method for the nitration of wood cellulose in somewhat thick pieces specifies a much higher percentage of nitric acid and a correspondingly lower percentage of sulphuric acid. The type of nitration apparatus used almost universally is one developed by Messrs. E. I. DuPont de Nemours in the United States during the war, in which one centrifugal takes the product from several (usually four) stirring vessels, called mechanical dippers. The latter are charged in turn with a measured amount of mixed acid at a controlled temperature, the charge of opened and dried cellulose is put in, and the mixture is mechanically stirred to ensure that the cellulose is completely wetted by the acid. At regular intervals the stirrers are emptied in turn into the centrifuge on the floor below, the excess of nitrating acid is spun out as completely as possible, and the pulp of nitrocellulose with its retained acid is discharged through a centre orifice in the base of the centrifugal into a stream of water in a drowning vessel below. The recovered spent acid is treated with the correct amount of revivifying acid to reproduce the original bath.

Nitrocellulose so prepared contains a small quantity of combined sulphuric acid, and it is customary to stabilise it by a short boiling process in dilute acid. The product is then thoroughly washed with water to remove all traces of the acid. A bleaching process is usually included in the washing. The nitrocellulose so obtained retains the fibrous nature of the original cellulosic material. The combination with nitric acid has, however, made it more resistant to water and increased its weight.

On account of the highly inflammable nature of dry nitrocellulose it is usual not to dry the product. After removing the excess of water by a centrifugal process (or sometimes by simple draining), the product is dehydrated with ethyl alcohol, either in a centrifugal machine or in a

special type of press in which alcohol can be pumped through the wet nitrocellulose under pressure. The product is a more or less dense cake of nitrocellulose containing from 30 to 45% of alcohol, which serves to bring the camphor into solution in the gelatinising process which follows. The spent alcohol, containing the water removed from the nitrocellulose, is redistilled and used again.

(2) Plastification of Nitrocellulose — The gelatinisation of nitrocellulose is almost invariably carried out with camphor, which when dissolved in alcohol possesses the property of converting fibrous nitrocellulose into a tough coherent transparent mass.

The quantity of camphor required by the industry is enormous, as it forms from one fifth to one-quarter of the weight of commercial celluloid. Natural camphor, *i.e.* the optically active product from the Formosan camphor tree, is still available, but it is a Japanese Government monopoly and owing to the growth of the Japanese celluloid trade it is not so freely available as it used to be. Artificial camphor, usually termed in commerce synthetic camphor, has been on the market for more than 30 years, and is made now in nearly all the principal celluloid-producing countries. In spite of prejudice against it among some celluloid users, it is weight for weight absolutely as efficient as the natural product.

The product obtained when nitrocellulose, camphor and alcohol are thoroughly kneaded in a warm mixer is a faintly yellow transparent dough. It is seldom used without some addition of colouring matter. If "colourless" transparent material is required a small addition of violet colouring matter is added to counteract the basic yellow. Coloured transparents are made by the addition of soluble dyes or finely dispersed pigment colours. Opaque materials require the use of various opaque pigments, such as zinc oxide, titanium oxide, artificial lakes, vermilion, prussian blue and various earth colours. The required standard of uniformity in colour is very high and the utmost care must be taken to obtain correct colour matching.

From the kneaders the dough goes to high-pressure filters where it is pressed through fine calico to remove small dirt and other insoluble impurities. The filter consists of a cylindrical charging compartment, jacketed with hot water and closed at the bottom by a thick perforated metal disc supporting a wire gauze and the filter cloth. The hydraulic pressure applied is approximately 6,000 lb. per sq. in., and the filtered material issues through the perforated disc in the form of long soft rods, which are collected in a suitable receptacle below the filter. The filtered material may either go back to the kneaders or may go straight to heated rolls where it loses alcohol and becomes harder. It then passes to slower calender rolls on which it is finally sheeted out in slabs about $\frac{3}{4}$-in. thick, which are cut to the size required for the final block. Several slabs are consolidated in a heated press, and on cooling a block of celluloid is obtained.

The block is sliced into sheets on a planing machine, in which the knife remains fixed during the stroke, while the bed of the machine to which the block of celluloid is attached moves to and fro in relation to the knife. The thickness of sheet is adjusted by the amount by which the knife is lowered between each stroke. The range of thicknesses for cut sheets of celluloid is normally from 5 thousandths to 500 thousandths of an inch.

Configurated patterns in celluloid are made by many different processes and combinations of processes. In some instances the pattern depends entirely upon blending materials of two or more different colours on the rolls. Pieces of different shapes and colours may be conglomerated by heating under pressure in the block presses. Imitation grained ivory is made by preparing two batches, slightly different in tint, running them out into thin sheets, making a pile of the sheets containing the two tints arranged alternately, compressing the pile into a block, and cutting it transversely. Of recent years imitations of mother-of-pearl have been popular. These are made by mixing into the plastic dough either a very fine metal powder in flakes or the so called pearl essence, a flaky crystalline material prepared from certain fish scales. The dough is extruded under pressure through a narrow slot and the flakes of metal or pearl essence align themselves parallel to the plane containing the long dimension of the slot and the direction of extrusion, producing a sheet which has almost a metallic sheen. There are various ways of breaking up and varying this sheen to produce the characteristic appearance of pearl. Composite materials in which one of the ingredients in a configuration is pearly are used considerably in the manufacture of fountain pens and propelling pencils.

(3) Finishing Processes.—The sheets cut from blocks by the planing machines still contain a certain amount of the original alcohol, and as the removal of this causes a shrinkage in volume it is necessary to dry it out in warm stoves. The time occupied by this seasoning process naturally depends on the thickness of the sheet. Thin sheets are seasoned in a few days, while sheets $\frac{1}{2}$ in. in thickness need several weeks. The temperature of seasoning is varied according to the material, but is usually about 35°C.

At the end of the seasoning stage the sheets still bear on the surface the parallel lines left by the knives of the planing machines. This is usually called a knife-line surface. For many purposes, for instance when the celluloid is to be moulded into articles at a later stage, this surface is quite satisfactory, but for other purposes, as for example, when making transparent sheets which are to have no further polishing treatment, a polish is applied to the full sized sheet by heating it under considerable pressure in contact with a highly polished metal plate. The sheet must be warmed to a sufficient temperature to allow it to take the surface of the polishing plate without "flowing," *i.e.* squeezing out to a larger area. This process needs extremely careful control. Matt metal plates are used to apply a matt surface in a similar way. The capital cost of block presses and polishing

presses is very heavy, and in Great Britain the manufacture has been unnecessarily complicated by the large number of sizes in which sheets are required. Each size needs a special block press and special polishing equipment. In the United States where there is a larger home market and less external competition, manufacturers have been able to standardise to a large extent on one size of sheet, namely 50 in. × 20 in. The size of sheet which is most economical to manufacture in this country is approximately 58 in. × 25 in. when polished and trimmed.

The manufacture of celluloid tubes and rods diverges from that of sheets at the rolling stage. Two types of tube-making machines are in use, and the choice between them depends on a variety of circumstances. Both employ extrusion of the hot plastic material through a nozzle fitted with a centred mandrel. In one type of machine the pressure is applied hydraulically, and in the other type by a geared screw. The hydraulic machine has a cylindrical barrel, and a cylinder of plastic dough to fit this barrel is made by rolling up a thin sheet off the rolls. This cylinder is placed in the barrel of the hydraulic machine and is pressed out by hydraulic pressure. In the screw machine celluloid in pellets is fed through a hopper on to a worm screw, mechanically driven, and the screw carries the material through the barrel of the machine, compacting it and finally extruding it as in the hydraulic machine. In both instances the process is one of continuous thermoplastic moulding.

Celluloid rods can be made in the same types of machine when required transparent or in plain colours. Configurated rods are usually cut from blocks by means of special attachments to the ordinary slicing machine. Many of the popular configurations in fountain pen barrels are made in this way.

In every celluloid factory there is a special department for dealing with scrap or waste celluloid. This material varies considerably in quality, as it may come originally either from first or second grade material, and in some processes it is possible to keep the scrap much cleaner than it is in others. It is one of the economic advantages of celluloid that the scrap material, when soaked in alcohol in a warm vessel, with or without the addition of more camphor, absorbs the solvent and becomes once again plastic. If this material is kneaded it rapidly becomes a plastic dough resembling new celluloid, and it is passed through the same operations.

Developments in celluloid manufacture during the last 10 years have mostly been in reducing the cost, and in improving the colour, transparency, and stability to heat and light.

Successful efforts have been made in U.S.A. to produce celluloid from nitrocellulose by a continuous process instead of in separate batches. A plastic dough of nitrocellulose, camphor, and solvent is filtered and continuously extruded through an adjustable slot. Special measures are taken to control the rapid shrinkage after extrusion. The sheet is seasoned in continuous lengths and sold in rolls in the unpolished state. This process yields a very clean product as the handling and exposure of the dough are reduced to a minimum. It needs a large and steady market in one type of celluloid, since changes of colour are not easy in plant of this type. The product is somewhat softer than ordinary celluloid, as a soft mixing is required for extrusion. The shrinkage is also somewhat different from that of sliced sheet celluloid, owing to the different incidence of the stresses set up in the seasoning process.

Properties of Celluloid.—Untinted celluloid to which no colouring matter of any kind has been added is a faintly yellow, transparent, tough colloid. Improvements in the colour of nitrocellulose during the past few years have given a celluloid which is not only practically colourless, but resists change of colour on exposure to light far better than was at one time the case. Hence the most delicate colours can be reproduced with a uniformity which is not possible in a material the basic colour of which varies.

The specific gravity of unpigmented celluloid varies somewhat with the camphor content (camphor being the lighter ingredient). The lower limit is about 1·35, and a highly pigmented sample may reach a density of 1·8 or more.

It is permanently thermoplastic, that is to say, it becomes soft on heating and rigid again on cooling. This change may be repeated any number of times, and lends itself to a large variety of moulding processes. Celluloid begins to be noticeably soft at a temperature of about 80°C., but commercial moulding processes are usually carried out at temperatures from 110°–125°C. Under these conditions, for instance, a rectangular blank of celluloid, cut from a celluloid sheet, may be moulded directly into a comb. Two sheets of celluloid in a divided mould may be blown out by compressed air introduced between them, producing a hollow moulded article firmly joined at the seams. Celluloid tubes may be softened in hot water and drawn over metal bars or tubes, giving a covering which shrinks firmly on to the foundation, forming a permanent protection for it. Celluloid may also be sawn, turned or drilled like wood. It resists water and moderately strong acid solutions, weak alkalis in the cold and practically all salt solutions. It is softened by acetone, amyl acetate, and generally by the carboxylic acid esters of low molecular weight, especially when mixed with alcohol. These are used in the preparation of celluloid cements. Saturated and aromatic hydrocarbons have no visible action, but long continued contact leads to some extraction of camphor.

The combination of properties just described explains the popularity of celluloid for toilet articles. The material is hygienic and washable, and delicate colours or blended colour schemes can be carried out with facility. Combs, hairbrushes, mirrors, tooth-brushes and shaving-brushes are made in large quantities. It is used for the manufacture of knife handles, since a very accurate imitation of natural ivory can be made, and the celluloid resists the conditions of ordinary domestic usage. The vogue of the

celluloid accumulator case depends on the resistance of the material to the hydrolytic action of sulphuric acid of accumulator strength. A celluloid accumulator case is lighter than a glass case and less liable to fracture. In the fountain pen trade, which is a comparatively new one, use is made of the facility with which attractive colour configurations can be produced, coupled with the resistance of celluloid to the action of ink. It is used for parts of various toys and games, the modern table tennis ball being an excellent illustration of how accurately the material can be moulded.

Transparent celluloid becomes doubly refractive when strained. Use has been made of this property to trace and measure the strains in engineering models by constructing them in transparent celluloid and examining them in polarised light. F. S.

CELLULOID PLASTICS.

PHOTOGRAPHIC FILM.

HISTORICAL.—In the following brief survey of the history of photographic film, mention is made of those processes and materials which may be regarded as having started an important industry. The photographic manufacturer is usually responsible for improvements in films themselves. In the case of special processes where the film manufacturer is not the original inventor, it is usually left to him to work out the method of making the film to suit the process. The first commercial introduction of flexible photographic films was due to Eastman who, in 1884, developed the roll film system of photography. The first films were of paper, oiled after development to render it transparent for printing. The paper was soon supplanted by stripping film, consisting of a paper base, a layer of collodion on which was coated the emulsion, and a layer of soluble gelatin between the paper and the collodion. The film was exposed in the camera in a special roll holder, and in 1888 Eastman marketed the first Kodak, using the stripping film in lengths giving one hundred exposures about 2½ in. in diameter. In 1889, Reichenbach, in Eastman's laboratory, was granted a patent for a method of making a transparent, flexible, rollable film of nitrocellulose, and in that year the first transparent roll film was marketed. The apparatus for coating the film base was patented in 1892. Edison purchased some of the first coating of this film in 1889, and used it in the first cinematograph camera, made by converting a Kodak. Thus the foundations of the cinematograph industry were laid. In 1887, Goodwin had applied for a patent, issued in 1898, for a method of making a cellulose nitrate support for photographic emulsions, but apparently Goodwin did not reduce it to practice. In 1884, Carbutt began the manufacture of film coated on thick, small sheets of celluloid, to replace plates of glass. This was not a flexible rollable film. In 1891, Eastman improved his roll film so that it could be loaded in daylight by the user. In 1892, he coated the film with a layer of gelatin containing conducting salts so as to eliminate the effects of the discharge of static electricity which occurred when the film was handled. In 1896, Eastman introduced the first positive cinematograph film. Prior to this, pictures had been made on negative film, which could be obtained in 100 ft. lengths, but it did not have adequate properties for projection. At this time, Eastman sold uncoated film base to certain experimenters in Europe, notably the Lumière brothers in France, who coated it with emulsion themselves. In 1903, Eastman introduced a film having a gelatin coating on the back to counteract curling tendency. It had been patented in 1890. Eastman commenced the manufacture of the first commercially practical safety film of cellulose acetate in 1908. In 1909, the additive Kinemacolor process of Smith-Urban was launched as the first commercialised process of cinematography in colours. The Gaumont additive colour process was put out in 1912. This and Kinemacolor failed after a relatively short life. In 1912, the Eastman Kodak Company put out cut sheet film and in 1913 the same Company introduced panchromatic negative cinematograph film on the general market, although they had previously made it for certain colour processes, notably the Gaumont process. The first suggestion of double-coated film for colour photography was made by Lewy in 1911, but it was not used commercially until 1912. The bipack method of obtaining two-colour separation negatives appears to have been first applied to cinematography by Brewster, in patents issued in 1915 and 1917. The original Kodachrome process was worked out by Capstaff in the Eastman Kodak laboratories in 1915, and about this time the first Technicolor films appeared, made by an additive two-colour process. Technicolor used a two colour subtractive process in 1923, two films being cemented back to back. In 1928, they changed to a two-colour imbibition process, and to the three colour process in 1933. In 1919, the Eastman Kodak Company introduced the modern type of double-coated (duplitised) X-ray film. In 1919, the Eastman Kodak Company started the practice of edge printing cinematograph film with latent footage numbers, and in 1921, they introduced films with tinted base. In 1923, the same company brought out 16 mm. reversal film and apparatus for amateur cinematography, and in 1928, commercialised the first colour process using lenticular embossed film—the Kodacolor process—which was followed in 1935 by Kodachrome, the first simple process of subtractive colour cinematography for amateur use. Colour film using a screen mosaic was put out by the Lignose Company and was followed by a similar film in the form of roll and cut sheet by the Agfa Company and the Lumière Company. The first cinematograph film in colours using a screen mosaic was put on the market by Dufaycolor in 1931. The Gasparcolor process of colour photography was first made available in 1934. In 1936, the Agfacolor process was put out. It is similar in its general principles to the Kodachrome process. The year 1928 marked a revolution in the cinematograph field with the commercial introduction of sound films.

CELLULOSE ESTERS FOR FILM.—At the present time photographic films are chiefly made of cellulose nitrate, or cellulose acetate in the case of the so-called safety film. In some cases the acetate contains a small percentage of nitrate or nitroacetate. Cotton is exclusively used as the source of cellulose. It is in the form of linters, which are the short fibres which remain on the hull of the cotton seed after the long fibres used in the textile industry have been removed. In the preparation of the cotton prior to esterification it is first mechanically cleaned to free it from dust, mineral particles, etc., and then degreased by heating under pressure with dilute alkali. It is then washed and bleached by careful treatment with chloride of lime or sodium hypochlorite, treated with dilute hydrochloric or sulphuric acid to remove the last traces of the bleaching material and iron, and washed again. The water is centrifuged off and the cotton is then conditioned to a uniform low moisture content.

In order to ensure satisfactory properties for coating in the form of thin film and adequate mechanical properties when finished, the cellulose must be nitrated with extreme care. The properties of the nitrocellulose obtained depend on the nature of the cotton, the composition of the acid mixture, the relative proportions of acid to cellulose, the temperature, and the time of reaction. Nitration is carried out with a mixture of sulphuric acid, nitric acid, and water, and to produce the greatest uniformity of product it is usually done in a nitration centrifuge. This ensures that all the cellulose particles come into contact quickly and simultaneously with the acid mixture. A nitration mixture stated by Clément and Rivière to give a good quality nitrocellulose consists of: sulphuric acid, 61·9%; nitric acid, 22·4%; water, 15·7%. For 280 g. of cotton, 10 kg. of solution are used at 40°C., and nitration lasts about 15 minutes. Nitration is so controlled that a nitrocellulose with a nitrogen content of 11·5–12·2% results. The viscosity is kept medium, and the product should be as colourless as possible so that the final film is clear and transparent. After nitration is completed, the nitrocellulose is centrifuged, very thoroughly washed, and bleached. Thorough washing is essential in order to remove all traces of acid, so as to ensure stability of the final film and freedom from action on the photographic emulsion which is coated on it. At the end of nitration the acid is run off, and the nitrocellulose is drained or centrifuged and passed to a washing vessel in which it is broken up and kept in motion for a long time. It is then stabilised in dilute alkaline carbonate or bicarbonate which neutralises the last traces of acid, an operation taking considerable time, then bleached in hypochlorite, treated with bisulphite and hydrochloric acid, and then very thoroughly washed again. After washing, the material is formed into cakes and pressed. It is stored wet until ready for use, when it is broken up and dehydrated with alcohol, the excess of which may be finally removed in a press or special centrifuge.

In the preparation of cellulose acetate, the hydrocellulose prepared from cotton is acetylated by acetic anhydride in the presence of a catalyst, usually sulphuric acid. In order to form cellulose triacetate, the theoretical proportions are 2 mols. of cellulose to 3 mols. of acetic anhydride. In this reaction, 3 mols. of water are formed and require 3 mols. more of acetic anhydride to combine with them. In practice a still higher proportion of acetic anhydride is necessary. In general, the proportions of the reactants are somewhat as follows: cellulose, 1 part; acetic anhydride, 4 parts; sulphuric acid catalyst, 0·1 part; as diluent, 4 parts of acetic acid are added. A large number of variations have been proposed to control the course of acetylation. Further, many catalysts have been proposed to replace or supplement the sulphuric acid. These include other mineral acids, acid chlorides, halogens, neutral salts such as zinc chloride, and organic salts such as hydrazine sulphate.

Acetylation is carried out in a mixing and kneading machine, the proportions of the ingredients being of the following order (Ulmann): cellulose, 20 kg.; acetic anhydride, 70 kg.; glacial acetic acid, 70 kg. About 2 kg. of sulphuric acid (66°Bé.) are added in small quantities at a time, the mixture being cooled to about room temperature. The reaction takes many hours, after which a product consisting mainly of cellulose triacetate results. When this is precipitated with water, it has an acetic acid content of slightly under the theoretical value of 62·5%. If it is desired to isolate the triacetate, the reaction mixture is poured into water, and a white fibrous mass separates, which can be washed free of acid and dried at about 40°C. In practice it is very rare that the triacetate is separated, since it is soluble in chloroform but not in acetone or methyl acetate. In order to produce the acetone-soluble variety it is necessary to reduce the acetic acid content to 52·6% or somewhat less by hydrolysis. To effect this, water, dilute sulphuric acid, or other reagents are added to the mixture in the acetylation vessel, the temperature and time of action being carefully controlled. The hydrolysed cellulose acetate is then precipitated from the acetic acid solution by pouring into water, centrifuged to remove the bulk of the dilute acid, washed thoroughly, dried, and ground up. In order to render the manufacture of cellulose acetate as economical as possible, the industry pays particular attention to the recovery and concentration of the acetic acid.

Another method for the production of cellulose acetate which is not used to much extent in the photographic industry gives the so-called fibrous acetate, in the preparation of which the cellulose fibres themselves are acetylated without going into solution. The reaction takes place in the presence of a liquid, such as benzene, in which cellulose acetate is insoluble. An objection to the product obtained in this way lies in the difficulty of carrying out the partial deacetylation uniformly through the mixture, the resulting acetate generally being only poorly soluble in acetone or methyl acetate.

Nitroacetate is used to some extent in the manufacture of film, and is prepared by the

acetylation of cellulose nitrate. Esters of higher organic acids than acetic acid, and mixed esters of organic acids, such as cellulose acetate-propionate, acetate-butyrate, acetate-stearate, etc., have been closely studied for use in film manufacture. The simplest general methods for the preparation of the mixed esters depend on the use of two acid anhydrides in the presence of a condensation material. Cellulose ethers and synthetic resins have been the subject of much investigation for use in making film, but they have not been used in practice up to the present time. Gelatin has been proposed, but has the disadvantage of swelling in water. Although this can be reduced by hardening, gelatin supports have not found favour. Casein has been proposed but never used, and much study has been devoted to cellulose regenerated from cellulose xanthogenate. Although it has good mechanical properties, it swells readily and undergoes deformation in aqueous photographic solutions, and often contains traces of residual sulphur, and is, therefore, not suitable for use in practice.

Film Base Compositions.—In the manufacture of film base in sheet form, the cellulose ester in solution is coated on a smooth surface in the form of a thin layer, and sets to a skin or film as the solvents evaporate. The skin is peeled from the surface, dried, and cured. The preparation of the solution involves : (1) selection of the solvent, which usually consists of a mixture of components of different volatility, including sometimes a non solvent ; (2) addition of plasticisers of low volatility to ensure that the finished film shall have flexibility and elasticity ; (3) filtration. An enormous number of patents have been issued for compositions and solvents for film coating solutions, or "dope" as they are called in the industry. The number of manufacturers of film base is very small—probably not more than ten—and the composition of the dopes actually used is in the domain of manufacturing secrets. They are, however, probably variants of certain general types. A typical solvent for nitrate is a mixture of methyl or ethyl alcohol with ether, or methyl alcohol and acetone, together with a third material, such as amyl alcohol, amyl acetate, or butyl alcohol to reduce the rate of removal of solvent on drying. In the absence of these high-boilers condensation of atmospheric water may produce so-called blushing. Other solvent mixtures contain aniline, methyl acetate, other esters, higher alcohols, various ethers, hydrocarbons, and oils. The plasticiser used practically exclusively with nitrate is camphor, in quantity depending on the desired characteristics of the finished product, but usually of the order of 10–20% of the weight of the nitrocellulose. Many other plasticisers have been proposed, including triphenyl and tricresyl phosphate (which also reduce inflammability), and castor oil is sometimes added. Clément and Rivière give the following formulæ : For coating on glass tables : nitrocellulose, 8 8% ; camphor, 3 02% ; methyl alcohol, 41·1% ; ether, 38·0% ; amyl alcohol 9 0%. For coating on a rotating wheel : nitrocellulose, 17·75% ; acetone, 88% ; amyl alcohol, 1 0% ; camphor, 3 25%. In the latter case, castor oil is sometimes added in amount not exceeding 5% of the weight of the nitrocellulose.

The properties of cellulose acetate vary so much according to the method of preparation that the choice of solvent and plasticiser cannot be given except in very general terms. The solvent most used is acetone, but among the many others which have been proposed and used in practice are methyl acetate, methyl formate, methyl ethyl ketone, chlorohydrocarbons, amyl acetate, diacetone alcohol, and ethyl acetate. The choice depends on the acetate and the method of coating the film base. It is common practice to add to the solvent a non solvent for cellulose acetate, such as alcohol and water, to control the rate of evaporation of the solvent when the base is coated. The most important plasticisers for cellulose acetate are the esters of orthophosphoric acid, particularly triphenyl and tricresyl phosphate. Others include esters of phthalic acid, monoacetin, diacetin, and triacetin, sulphones and sulphonic esters. Mixtures are generally employed. Many other additions have been proposed, such as dyes to control the colour of the film, nitrocellulose, fillers, and ultra-violet absorbing materials. Although in many ways the preparation of cellulose acetate film base resembles that of cellulose acetate sheeting for other purposes, the choice of materials used in the manufacture is restricted by the fact that the material is ultimately to be coated with photographic emulsion, which is extremely susceptible to the action of traces of many chemicals. For coating, the solution contains 12–16% of acetate, and the plasticiser is present in amounts up to about 40% of the dry cellulose acetate, the actual amount depending on circumstances.

After the solutions of cellulose nitrate or acetate are prepared in proportions suitable for coating, they are carefully filtered under pressure in order to ensure complete transparency and uniformity of the finished film base. Bubbles of air are removed and the filtered dope is stored in containers from which it can be piped to the coating machines.

Coating Film Base.—Of the two methods for preparing a film from the solution of cellulose esters, evaporation of the solvent or precipitation, only the former is used to any extent in practice. The solution is coated on a polished surface, uniform so as to avoid irregularities in thickness of the film, and is stripped from the surface when it is strong enough to be handled The earliest films were coated on horizontal plate glass tables, up to 200 ft. long, about 3 ft. 6 in wide, and made of separate sheets of plate glass cemented together end to end. The dope was applied from a trough with a spreader, which was slowly moved along the glass table from one end to the other. After coating, the table was covered in such a way that it was in a channel through which air was passed to draw off the solvents. Nitrocellulose film from ether-alcohol required about 6 hours for drying, while cellulose acetate from acetone required much longer. The photographic emulsion was usually coated on the film base before it was stripped from the glass. Coating film base on glass

tables had a number of drawbacks, chief of which were the difficulty of obtaining material of uniform thickness and the limit to the length of base which could be coated. Although this was satisfactory for small films such as cut film and roll film, it was unsatisfactory for cinematograph film because several splices would be required to make up the lengths of 1,000 ft. or more used in cinematograph practice. Glass tables are no longer used for film base manufacture.

Film base coating machines used at the present time have a rotating endless polished surface on which the base is coated, and from which it can be stripped continuously so as to provide single lengths up to 2,000 ft. in length. Two types of rotating machine are employed. One of these (Fig. 1) uses an endless metal band of polished copper, nickel, or silver some 26 in. wide and 40 ft. or more long, supported in a horizontal loop between two drums one of which is driven. The other type (Fig. 2) consists of a metal drum, wheel or ring with a wide, flat, polished rim, driven about an axle, or by wheels or rollers which support it internally, or from below externally. The drums are made up to about 20 ft. in diameter, and the surface is of iron or copper on which is plated silver, nickel or chromium, polished so as to give a surface of a high degree

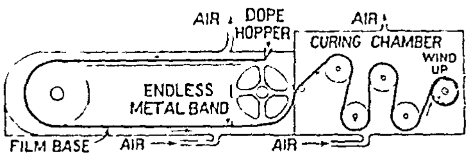


Fig. 1.—Diagram of Band Coating Machine for Making Film Base.

of regularity. Sometimes a polished surface is supplied by coating the metal with a layer of gelatin containing some glycerin and methyl alcohol. This is usually done with the band machines. The coating band or drum is enclosed in a housing through which air is circulated to permit the solvents to evaporate. They are drawn off and carried to a recovery plant. The dope is applied to the band or drum from a stationary trough provided with a spreader, the dope being fed to the coating trough by pipe line from the storage tanks. The band or drum, which may be heated internally, is rotated very slowly so that after it has made practically a complete revolution, the film can be stripped off and then passed over a number of small heated drums, to be finally wound up on a shaft at the end of the machine. The rotational speed of the drum depends on its size, the amount of dope coated, the rate of circulation of the air and its temperature. Drum machines used in practice give film base up to nearly 60 in. wide and 2,000 ft. long. The bulk of the film base manufactured in the world at the present time is made on drum machines. The same types of machine are used for coating both nitrate and acetate base, although the rate of rotation of the machines and the temperature of the drums are determined by the nature of the material coated. Extreme care is taken to ensure freedom from dust and other impurities, and the surface of the drum is so prepared and the machine operated with such regularity as to ensure the utmost uniformity of thickness of the coated base. The thickness of the film is determined by the viscosity of the dope, the type and adjustment of the spreader, and the rate at which the drum is rotated. Film base used in practice varies in thickness according to the purpose for which the film is to be used, ranging from about 3/1,000 in. in the case of roll film to about 8/1,000 in. for cut sheet film. Special precautions are usually taken to prevent the building up of charges of static electricity in the machine, and the concentration of solvent vapours is kept below the explosive limit so that there will be no danger of explosion if a static discharge occurs. Before it is stripped from the drum the film may be subjected to treating solutions to modify its curling tendency, or change its colour, resistance to moisture, electrical properties, etc. While it is passing through the curing chambers, it may be treated with baths, such as water, to remove a small percentage of residual solvent

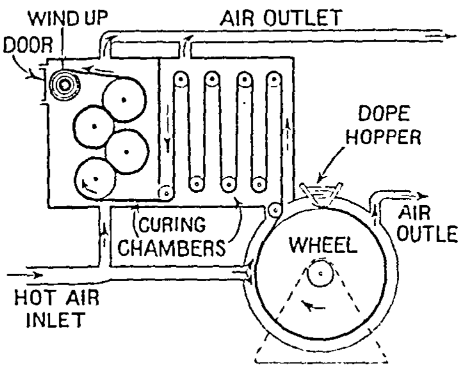


Fig. 2.—Diagram of Wheel Coating Machine for Making Film Base.

or other constituent of the dope, or through solutions or liquids which modify its molecular structure.

When the band or drum is coated with a gelatin layer to provide the smooth surface on which the dope is coated, the surface can readily be renewed at intervals by recoating with gelatin. In the case of those machines in which the cellulose ester solution is coated directly on polished metal, the metal surface itself must be renewed periodically by electroplating and polishing. The handling of the very heavy drum for replating and polishing is a difficult task requiring extreme care, and usually there is an electroplating department directly associated with the film-base-making department for carrying out this work. Another auxiliary plant which operates directly in conjunction with the base-making plant is that for solvent recovery. Many processes for solvent recovery are used in practice, including adsorption by sulphuric acid, active charcoal, silica gel, and the Brégeat cresol method.

Preparation of Base for Emulsion Coating.—In the processing of photographic film,

it is passed through a number of aqueous solutions which cause the gelatin of the sensitive emulsion to swell and tend to strip from the support. If it is coated directly on cellulose nitrate or acetate, it will strip very readily, even before it has been treated in aqueous solutions. It is, therefore, necessary to prepare the support in order to ensure adhesion of the emulsion. This is done in a number of ways, either by some treatment of the surface of the film base itself or by coating it with a thin layer of material known as a substratum, or "sub" The treatment varies according to the character of the nitrate or acetate employed. It has been proposed to hydrolyse the surface of the film by means of dilute acid or alkali, and to coat it with a layer of weak collodion, silicate, gelatin, plain or bichromated, or invert albumen in alcohol The usual practice, however, is to coat the base with a solution containing gelatin which is made to adhere to the support by solvents for the support. When a gelatin layer of satisfactory adhesion is applied, the emulsion itself will stick to the gelatin, which thus acts as an adhesive binding emulsion layer and support together. A typical sub will contain the following ingredients (1) an adhesive, usually gelatin, (2) a solvent for the adhesive, generally water, and stabilisers, such as organic acids, (3) solvents for the support tending to dissolve it or cause it to swell, such as methyl and ethyl alcohol, acetic esters, acetone, acids, etc. In some cases, particularly that of cellulose acetate, it is necessary to use multiple sub coatings, the first one being, for instance, of cellulose nitrate, in a very thin layer Since the sub contains solvents and non solvents for both the cellulose ester and gelatin, it is necessary to select the relative proportions of the constituents with extreme care Moreover, they must be of such a nature and degree of purity that they do not adversely affect the emulsion to be coated on them The sub is usually applied on the film as it comes from the base making machine. It is applied in an extremely thin layer by immersing the film in it, or by an application roller, and is dried by cold or warm air

Certain films, used mainly in the photo-engraving industry, and known as stripping films, are deliberately made so that the emulsion layer can be stripped from the base, usually of paper, and transferred to another support, such as glass. These are of two kinds, dry stripping and wet stripping films. The emulsion layer in the case of the former can be readily peeled from the base after processing and drying. In the wet stripping films, the emulsion layer comes away from the support in the fixing bath or wash water The emulsion is generally coated on a thin "skin" of hardened gelatin, cellulose nitrate or acetate, to give it sufficient rigidity for handling after stripping. This skin must be permeable to water in the case of wet stripping film. It is cemented to the support by an adhesive which holds it in place until stripping is desired. Such a cement may contain resins in the case of dry stripping film, or soluble gelatin in the case of wet stripping film.

EMULSION COATING.—The photographic sensitive layer, known as the emulsion, which is coated on the prepared film base, consists of a suspension of silver halide in gelatin. In the case of negative films the halide is silver bromide containing a few per cent of silver iodide. Films used for preparing positive transparencies usually have silver bromide as the light sensitive medium, and in some cases this has a very small content of silver iodide. Some special films used in the photo engraving industry consist mainly of silver chloride in gelatin. The silver halides are present in the form of minute crystals, the size distribution of which varies according to the nature of the emulsion. The largest are in negative emulsions, and may range up to 3-4μ in diameter. The silver salts are precipitated in a warm liquid gelatin solution, and undergo a series of digestion and ripening processes as a result of which the emulsion gains the desired sensitivity to light, and the ability to reproduce tone values in the required way. Special additions are made to the emulsion to cause it to harden after it is dried, to give it the correct surface tension to enable it to be coated uniformly on the film base, and to ensure suitable keeping quality If it is desired to make the emulsion respond to light of wave lengths other than the ultra violet, violet, and blue to which the silver bromide is itself sensitive, dyes of the cyanine class are added. The concentration of the gelatin in an emulsion ready for coating on film varies according to the purpose for which the film is to be used, but a figure of 9% may be taken as typical Similarly, the ratio of silver salts to gelatin varies, but 3 parts of gelatin to 1 of silver halide is a common ratio.

The steps involved in preparing emulsion coated film are. (1) coating the emulsion, (2) chilling to cause the gelatin to set as soon as possible after the emulsion is applied to the film, (3) drying. In an emulsion coating machine (Fig. 3), the roll of film base is arranged at one end and the film passes continuously round a roller which dips into a trough of warm, melted emulsion, or which is in contact with an application roller which itself dips into the emulsion The emulsion, previously melted, is fed continuously to the trough, at a suitable temperature After the emulsion is applied, the film is passed round a chilled cylinder of large diameter or through a chill box in which cold air cools the gelatin so that it sets rapidly and has no tendency to flow during subsequent operations. When the setting is complete, the film is looped by a mechanical device on to long rods or sticks which travel slowly and horizontally down a long drying alley supplied with conditioned air. The festoons of film, some 8 or 9 ft. deep, travel bodily along the alley, and as drying proceeds, the temperature of the air is slowly and progressively raised until the emulsion coating is dry. Then the temperature further along the alley is allowed to fall gradually, until the coated film is finally reeled into large rolls, and then put into light tight boxes where it is stored prior to cutting into sheets or slitting into rolls. Great care is taken in coating the emulsion on the film base to ensure perfect uniformity of thickness of the coating. The thickness itself is regulated as desired by varying the viscosity of the emulsion by controlling its temperature,

and by appropriately selecting the speed of coating. The rate and uniformity of drying of the film play an important part in determining its properties, so that the air in the drying alley is carefully conditioned as to humidity and temperature, a recirculating system being generally employed. The air is kept scrupulously clean by scrubbers, washers, and filters, since the photographic emulsion is very sensitive to dust, particles of metal such as iron and copper, sulphur, and gaseous impurities such as hydrogen sulphide, nitrous oxide, etc. ; further, abrasion of the film surface and static electric discharges must be avoided, since these produce markings on the film when it is developed.

Another type of emulsion coating-machine has been used in which the film is not dried in loops, but is gripped at the edges and carried horizontally through the drying tunnel. In a machine of this type, the film can be coated on both sides, which are dried simultaneously. In the normal type it is usually necessary to coat and dry one side first and then follow with the other. In present-day film manufacture, many films carry more than one coating, either on one or both sides of the base. Some double-coated

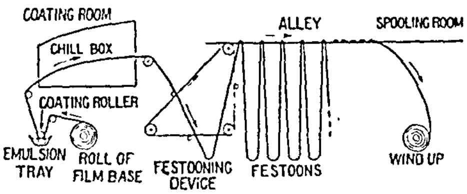


Fig. 3.—Diagram of Film Emulsion Coating Plant.

films carry two superimposed emulsion coatings on one side, the lower being an emulsion capable of giving high contrast, while the upper is a fast emulsion of lower contrast. The double coating extends the exposure latitude of the film. The most complex multiple-coated film is of the type used in the Kodachrome process of colour photography. Three emulsions are coated on one side of the base and are separated by gelatin intercoatings, making five layers in all. The total overall thickness is about equal to the thickness of a single normal coating, *i.e.*, about 8/10,000 in. It is possible to coat emulsion on film in a layer less than 2/10,000 in. thick, and of such a high degree of uniformity that no effects due to thickness variation can be picked up photographically.

Special Coatings.—Many films have the emulsion layer overcoated with a thin layer of gelatin to protect them against the effects of abrasion. Some films, such as those employed in certain processes of colour photography, and in X-ray photography, have emulsion coated on both sides of the base, and may, in addition, be overcoated with gelatin. In addition to the emulsion and its overcoating layer, other coatings are applied to film for special purposes. The so-called N.C. or non-curling coating is a layer of gelatin applied to the side of the base opposite to that carrying the emulsion, to offset the tendency of the film to curl when the emulsion is dried after development. Coatings are also applied to counteract halation, or spreading of the image due to multiple reflections inside the support. These layers are intended to reduce the intensity of the photographically effective light reflected back into the emulsion from the back side of the base. They are very often of gelatin containing dyes which absorb much of the light to which the emulsion is sensitive. For example, in the case of the so-called orthochromatic films, which are sensitive to blue and green, the antihalation dye is red in colour. A black dye would be best suited for panchromatic films, which respond to all visible colours. No black dyes are known, however, which are suitable from all points of view, and it is customary to employ a high density of green dye. Mixtures of dyes have also been proposed, the absorption maximum of one corresponding to the absorption minimum of the other. The dyes must have the property of bleaching in one of the solutions used in processing the film after exposure, and they must not affect the properties of the developer, nor the emulsion with which they are in contact when the film is rolled. Antihalation layers of gelatin containing dyes also serve the purpose of non-curling coatings. In some cases, particularly that of negative cinematograph film, a black antihalation layer is applied integrally with the back side of the base. This dye is not bleached in processing, but since it is used only on negative materials, its presence in the finished film merely serves to increase somewhat the exposure required in printing. In addition to dyes, other materials have been used as antihalation layers, notably manganese dioxide, which has been used between the emulsion and the base, but is usually employed coated in gelatin on the back side of the film. Dyes have been applied to the back of the base without the use of any colloid medium like gelatin, being coated from a solvent and buffed after drying. Dyes in gelatin are sometimes overcoated on the emulsion or on the back of the base to act as light filters in film for colour photography. Other coatings which have been applied to the back of the film are gelatin layers containing inert salts to render them electrically conducting in order to prevent the accumulation of charges of static electricity when the film is handled, and gelatin layers containing some diffusing material to permit retouching.

Special Films.—Various types of film support are available for special purposes. During the first 30 years of film manufacture, cellulose nitrate film was used practically exclusively. Since the War, however, the use of acetate film has been steadily increasing, although nitrate is still used almost entirely in the professional cinematography industry. Cellulose acetate film has the great advantage of low inflammability, presenting a hazard which is no greater than that of newspaper or the textile materials which are in common use. However, in the past, it was considered to be unsuited for many purposes since its physical and mechanical properties were not equal to those of nitrate film. In recent years much improvement in its properties has been attained, and it is finding increased use, particularly where the fire hazard offered by nitrate film is a serious drawback.

For instance, acetate film is used exclusively for substandard cinematograph film which is used by amateurs in the home, and in schools, and also for cinematograph films of standard 35 mm width employed for teaching purposes. The bulk of X ray film is on acetate base, and there is a rapidly growing use of acetate for film used for professional photography, particularly in the United States

Film used for topographic survey and mapping purposes should have the minimum of shrinkage, which should be equal in both directions. The base used for such film, for example for aerial cameras, is largely of the low shrinkage variety, the characteristics being produced by special treatment during manufacture Paper is notoriously variable in its dimensional characteristics, and for mapping and other purposes where dimensional variations must be kept to a minimum, substitutes for paper have been made consisting of low shrinkage film base in which a white pigment is incorporated. Another material for the same purpose consists of paper with a thin sheet of aluminium laminated in it. In the cinematograph industry it has been common practice to use film on tinted base so as to give the projected picture a colour supposed to be in harmony with the feeling of the picture For this purpose, dyes are incorporated in the support With the introduction of sound films, care had to be taken to ensure that the dyes used for tinting the base did not absorb the radiations which it was necessary for the film to transmit to the photo electric cell used in the sound reproducing equipment With the present practice of using cells having their response mainly in the infra red this problem is easier of solution, since there are relatively few dyes which have strong infra-red absorption. Films which are to be used for display purposes in illuminators are sometimes made translucent by the incorporation of white pigment. Base for X-ray film has been dyed blue to enhance visual contrast when the film is viewed. Special films have been made for mechanical methods of sound recording in which the film base is coated with an opaque layer which is readily scratched by a stylus For cinematography it has often been proposed to reinforce the edges of the film in various ways in the attempt to increase its projection life, but this is not done to any extent in practice Films have also been made in which a bright metallic reflecting layer is coated between the base and the emulsion to enable projection to be carried out by reflected instead of transmitted light. One of the earliest attempts to make a "safety" film was done in this way, the support being of paper. Projection by reflection is not carried out in cinematograph practice. So called waterproof paper, made by impregnating paper with a solution of cellulose nitrate, is used in apparatus from which it is desired to deliver developed and dried prints in the shortest possible time, such as automatic cameras used for portraiture, and also where it is desired to reduce the shrinkage of the paper itself. For the purpose of increasing the mechanical strength of film it has been proposed to laminate several layers of thin base. This has been done, for instance, in the case of films of regenerated cellulose, and although it results in a product of exceptional mechanical strength, the dimensional variations which such a material undergoes when it is handled in photographic processing solutions prevent its use in practice. Films have been made in which the support itself is sensitised instead of being coated with a gelatin emulsion. For instance, silver bromide has been precipitated in a film of regenerated cellulose by bathing it successively in silver nitrate and potassium bromide. Such a preparation has such a low sensitivity that it can but rarely be used in practice. Regenerated cellulose films have been sensitised in the mass by light sensitive diazo compounds in the presence of coupling components. The diazo compound is destroyed by light, and when the film is made alkaline, as in an atmosphere of ammonia vapour, the unchanged diazo material links up with the coupler and gives a direct positive dye image. Film of this kind is used to some extent in practice. It usually has such a thin support that a special type of projector is required to project it It has also been proposed many times to sensitise film with bichromated gelatin instead of a gelatin silver halide emulsion, but such films do not find favour, on account of their low sensitivity. For colour photography, it has been proposed to hydrolyse the surface of a cellulose acetate film and sensitise it with bichromate Such a film, exposed to short wave length light, shows differential absorption for dyes so that a coloured image can be obtained. Thin collodion films carrying a layer of gelatin incorporating a pigment have been used for colour photography, the gelatin being sensitised before use by bathing in bichromate solution.

Colour Photography—A number of different types of film are used, according to the process It is only in the case of films which serve as the final or intermediate support for the coloured image or one of the partial colour images that special properties are required. The films used for preparing the negatives or positives employed for making a colour print on some other material, and not required to carry any of the colours themselves, are of the same type as used in normal photography, although the emulsion or support may carry filter dyes and antihalation layers, and may be sensitised to colour by means of sensitising dyes. In the case of films on which gelatin relief images are prepared from the separation negatives, and stained with dyes to give a colour transparency by mounting in superposition, or a colour print on paper or film by transferring the dyes from the reliefs by imbibition, it is necessary so to prepare the support or substratum that it is not stained by the dyes. If it is stained, the high lights and whites of the colour print will also be stained In the so called screen unit processes of colour photography, the film carries a mosaic of minute dyed elements between the emulsion and the support. These are placed on the support either by sprinkling on coloured particles, or by ruling, or photographically printing through fine line screens. In the first case, the film is coated with an adhesive layer, and on this are sprinkled minute particles dyed blue, green,

and red. The Filmcolor process of Lumière employs dyed starch grains, which are rolled flat and the interstices between them filled with a black pigment. The Agfa Ultra Colour film is prepared by using small dyed resin particles which are rolled so that they come into contact at the edges, and no black filling is required. The Dufaycolor film employs a screen made of dyes, the proper balance of the three colours being obtained by dyeing uniformly in one colour, ruling a fine line resist, bleaching the dye between the resist, applying a second dye followed by another resist, and so on. After the screen has been applied to the support, it is varnished to isolate it from the emulsion which is coated on it. In the so-called lenticular film processes of colour cinematography, first made available commercially in 1928 in the Kodacolor process, the back of the film base is embossed with minute lenses. In the first films these were 22 to the mm., but later the number was increased. The lenses are cylindrical, running lengthwise along the film, and are embossed in the film base, warmed to soften it, by suitably shaped embossing cylinders. The lenses are made with a high degree of precision and have their focus in the opposite side of the base. Although this method of cinematography in colours enjoyed considerable success in the substandard, amateur field, it has not been adopted in the professional field.

Finishing, Cutting, Packing Film.—Film is used in the form of flat sheets or rolls. The material from the emulsion coating machines may be in any size up to the width of the base as made and some 2,000 ft. long. It is transferred to a slitting machine where it is slit accurately to the desired width by rotary knife blades. As it passes from the roll to the slitting knives it is inspected and all visual defects are marked by sticking a patch on them so that the defective part can be detected later and removed. If sheet film is being prepared the slit rolls are cut across at intervals to give the desired size of sheet. They are then assembled with interleaving sheets of black paper, and the desired number of sheets is wrapped in tinfoil and black, red, or green paper, and packed in boxes. In the case of film packs, the interleaving paper is struck to one end of the sheet of film, and carries a long projecting portion which serves to pull the film round in the pack after it has been exposed. Twelve sheets are assembled with pressure plate and light trap, and inserted in a metal or card container which is wrapped and put in a box. Humidity is carefully controlled in all finishing rooms—usually to 70% relative humidity. Cut film is usually obtainable in any desired length, and widths up to about 40 inches.

The two chief kinds of film used in the form of rolls are roll-film and motion picture film. Roll-film is used in the great majority of amateur cameras and is made so that it can be loaded in the camera in daylight.

Cinematograph film is 35 mm. wide and is provided with perforation holes along the edges so that it can be driven through the camera and projector by toothed sprocket wheels and claws. In projection the film image may be magnified over 300 times linearly on the theatre screen. Since the picture must appear perfectly steady to the audience, great precision is necessary in the dimensions and spacing of the perforations. The slitting of the film is done with revolving knives, equally spaced above and below the film to get a shearing action, the upper knife having a keen razor edge and the lower knife a square edge. The perforation is carried out by punches and dies ground with such precision that the punches cannot be inserted in the dies by hand without injury. Each punch consists of eight punching members, and eight positioning members which have tapered ends and fit the holes previously punched so as to position the film exactly for the next set of holes to be made. The slit and perforated film is wound on wooden or metal cores in lengths up to 2,000 ft., wrapped in black paper, and packed in tin boxes which are sealed with tape. In addition to the 35 mm. film used for standard cinematograph practice, there are in common use three substandard widths of film, 16 mm., 9·5 mm., and 8 mm., usually wound on metal reels and packed in tin boxes. Films are distributed all over the world, and international standardisation of dimensions of film and apparatus is therefore necessary. This has been carried out in the case of 35 mm. and 16 mm. film. The earliest work was done by the Society of Motion Picture Engineers in the United States, and the International Congress of Photography, and later in co-operation with the International Standards Association, and national standardising bodies. The internationally adopted slitting and perforating dimensions of negative and positive raw film of 35 mm. and 16 mm. width are shown in the illustrations (Figs. 4 and 5). The dimensions apply to the fresh material immediately after slitting and perforating. Standards have also been adopted for film splices. In addition, there are standards for sprockets, camera, and projector apertures, sound scanning beam and sound track, frame lines, sound film speed, position of the sound record relative to the picture aperture, projection lenses, and lantern slide mat openings.

When film is being slit for cinematograph purposes, it is customary to expose it on the edge to a stencil which prints some identification markings and numbers indicating the footage. These marks appear as black when the film is developed. Sometimes edge markings are printed in such a way that they are visible before development. The footage numbers are used as a guide in assembling and editing the films, particularly sound films, where the sound record is made on one film and the picture negative on another, the two being printed in combination on a single positive film.

Certain types of film prepared in rolls are provided with leaders and trailers, of paper, film, or film base. These permit threading of the film in cameras and projectors, and may serve as a protection against light.

Cinematograph films for projection in theatres are usually lubricated before use by the application of a solution of wax in carbon tetrachloride. To remove the dirt and grease which accumulate on the films in use, they are cleaned

with carbon tetrachloride, buffed, and polished. Many varnishes and processes have been proposed for removing or obliterating scratches on cinematograph film, and a large number of patents have been taken out for varnishes and processes for treating film so as to prolong its useful projection life.

In the editing and repair of cinematograph films it is necessary to join films together end to end. This is done in a splicer made with such precision as to ensure correct relationship between the perforations each side of the splice. The cement used for splicing contains an adhesive and softeners for the cellulose ester, and thus differs according to the nature of the film base. Before making the splice the emulsion must be removed from one of the films. No cement is known by which a satisfactory splice can be rapidly made between the base side of one film and the gelatin coated side of the other. The splice must be strong enough so that it does not provide a weak point in the film.

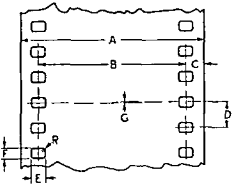


FIG. 4.—STANDARD 35 MM. FILM. CUTTING AND PERFORATING DIMENSIONS OF NEGATIVE AND POSITIVE RAW STOCK, APPLYING TO MATERIAL IMMEDIATELY AFTER CUTTING AND PERFORATING.

	Millimetres	Inch equivalents
A	35·00 $+0·00$ $-0·05$	1·378 $+0·000$ $-0·002$
D	4·750 $\pm$ 0·013	0·1870 $\pm$ 0·0005
E**	2·794 $\pm$ 0·01	0·1100 $\pm$ 0·0004
F**	1·98 $\pm$ 0·01	0·0780 $\pm$ 0·0004
C	3·40 $\pm$ 0·05	0·134 $\pm$ 0·002
B	28·17 $\pm$ 0·05	1·109 $\pm$ 0·002
G	Not $>$ 0·025	Not $>$ 0·001
L*	475·00 $\pm$ 0·38	18·700 $\pm$ 0·015
R**	0·5	0·020

* L = the length of any 100 consecutive perforation intervals

** This single style of perforation, known as the SMPE perforation, shall be used for all 35 mm film It is the same as the perforation known prior to July 14, 1933 as a standard positive perforation

These dimensions and tolerances apply to the material immediately after cutting and perforating

In all operations involving the handling of sensitive film in the open, the rooms are illuminated with light of a colour by which the film is not affected in the short time it is exposed. In the case of non-colour-sensitive film, the light is yellow, orange, or light red. With green-sensitive, orthochromatic films, it is deep red. With panchromatic films, a very low intensity of green light is used. Although such films are sensitive to all colours, green is selected because it is the colour to which the eye is most sensitive. For a given visibility, a lower intensity of green light can be used than of any other colour, and any effect on the film is thus reduced to a minimum

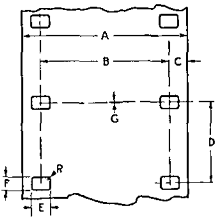


FIG 5.—STANDARD 16 MM FILM CUTTING AND PERFORATING DIMENSIONS OF NEGATIVE AND POSITIVE RAW STOCK, APPLYING TO MATERIAL IMMEDIATELY AFTER CUTTING AND PERFORATING

	Millimetres	Inch equivalents
A	16·00 $+0·00$ $-0·05$	0·630 $+0·000$ $-0·002$
D	7·620 $\pm$ 0·013	0·3000 $\pm$ 0·0005
E	1·83 $\pm$ 0·01	0·0720 $\pm$ 0·0004
F	1·27 $\pm$ 0·01	0·0500 $\pm$ 0·0004
C	1·83 $\pm$ 0·05	0·072 $\pm$ 0·002
B	12·320 $\pm$ 0·025	0·485 $\pm$ 0·001
G	Not $>$ 0·025	Not $>$ 0·001
L*	762·00 $\pm$ 0·76	30·0 $\pm$ 0·03
R	0·25	0·01

* L = the length of any 100 consecutive perforation intervals

These dimensions and tolerances apply to the material immediately after cutting and perforating

FILM QUALITY CONTROL TESTS.—Chemical, physical, and photographic tests are used to control the properties of film.

Chemical Tests: for the control of raw materials used in the manufacture of film base, emulsions, packing materials, materials for the construction of handling machinery, chemicals used in processing exposed film; control of the finished film base to determine probable effect on the emulsion, stability, and physical properties.

Physical Tests: of greatest importance in the case of cinematograph film which is subjected

to considerable mechanical strain in use; dynamometer tests for elongation, yield point, breaking load; folding resistance; elasticity; wear and tear tests in the projector; impact tests for strength at perforations: resistance to water; expansion when wet, shrinkage when dried; effects of humidity and temperature, including extreme heat and cold; strength at splices; inflammability and rate of burning; resistance to photographic processing solutions; thickness and uniformity of thickness; ageing tests; control of colour of tinted films, anti-halation and filter layers; transparency, freedom from colour, haze, spots, and markings; hardness and abrasion resistance; viscosity of dopes and emulsions; jelly strength, setting and melting-points of emulsions.

Photographic Tests: sensitometric tests to determine photographic speed, contrast, rate of development, photographic quality, fog; colour sensitivity; special tests for graininess, resolving power, image sharpness; keeping tests under various humidities and temperatures; defects, such as static and abrasion marks, dirt, spots, etc.; uniformity of sensitivity; tests of suitability for special purposes.

Recovery of Film Base and Silver.—An important economic factor in the film industry is the recovery of scrap film base and the silver in the emulsion coated on it. In the recovery of the base, the gelatin emulsion is removed by breaking it down by the action of enzymes, weak alkali, or sodium hypochlorite solution, scrubbing and washing. The recovered base is used for a variety of purposes, chief among which is the manufacture of cellulose ester lacquers. The silver or silver bromide from the gelatin layer settles in the tanks used for removing the gelatin, is separated and dried, and the silver is recovered by the usual metallurgical methods. Silver which is present in solution, as in fixing baths, wash waters, etc., may be precipitated as silver sulphide, or recovered directly as silver by precipitation by zinc, or by electrolysis. In the cinematograph industry large amounts of metallic silver of good grade are removed from used fixing baths by electrolytic methods, and the baths regenerated for further use.

Ageing and Storage of Film.—Film base made of cellulose esters undergoes small dimensional changes on handling or storage, unless specially prepared in manufacture. These changes are irreversible and reversible. The irreversible changes are due to the loss of small amounts of volatile materials which remain in the film after manufacture. The loss of these, on keeping the film or passing it through solutions, results in a slight but permanent contraction of the film. By efficient curing during manufacture these volatile residues may be eliminated and the irreversible shrinkage thus reduced to a minimum. The reversible change is due to gain and loss of moisture, and is usually greater at right angles to the direction of coating the film base than in the coating direction. It is greater with acetate than with nitrate film. It is analogous to the case of wood, which swells in water across the grain to a greater extent than in the direction of it. By rigid control in manufacture it is possible to reduce such a dimensional change to a minimum and to render it practically equal in both directions. In recent years there has been a marked diminution of dimensional changes in commercial film, and in the case of some special films made for topographic purposes the changes are negligible.

The life of photographic film depends on the quality of the film base, the treatment and handling of the film in processing and use, and the method of storage. Two problems are involved, *i.e.*, the keeping of the photographic image, and the keeping of the base. These two are inseparably connected, the one being able to influence the other. To ensure maximum stability of the image, ignoring for the moment the effect of the support, fixation and washing must be very thorough. The normal fixing bath should be followed by one which is unused, or which has a dissolved silver content of less than 1 gram per litre. The film should then be thoroughly washed in tap water until the thiosulphate content is reduced to below 0·002 mg. per sq. in., and then treated in changes of distilled water until the thiosulphate is less than 0·001 mg. per sq. in. It should then be thoroughly dried. Film should be stored in an atmosphere free from impurities which will affect the image, particularly traces of hydrogen sulphide, hydrogen peroxide, ozone, and nitrous oxide. It is not possible to make definite statements about the possible life of film base, since film has been known for only a relatively short period. A few general statements can be made, however, about the probable changes which film can undergo with age, and the conditions which will tend to reduce these to a minimum. This problem is of great importance for film archives, libraries, and so on. Cellulose nitrate is an inflammable material which is not as stable as cellulose acetate. Cellulose acetate is slow-burning, presenting a fire hazard no greater than ordinary paper, and is relatively stable chemically. Deterioration of the nitrate is accelerated by increasing temperature or humidity, by raising the pressure, by incomplete fixation and washing of the photographic layer, and by the products of its own decomposition. It is not known that any decomposition products from acetate have an adverse effect on the keeping of acetate film. Both kinds of film tend to shrink with age, and acetate film gets brittle at low humidities. Its flexibility can be restored by rehumidifying. In those conditions which tend to favour decomposition of nitrate film, the traces of decomposition product, chiefly nitrous acid, may exert a destructive action on the gelatin coated on it, as well as on the silver image.

The method of storing will depend on the length of time to elapse before the film is to be used. In the case of archives, where the film may lie undisturbed for a long period, the best conditions of storage demand low temperature and dryness. If the records are on nitrate base, the best practice would be to copy them on to acetate film of low shrinkage, and store the acetate film. Otherwise it would be desirable to examine the films at intervals of a few years, and if visible changes are occurring, or the film is shrinking so that it cannot be run through a

cinematograph printer or projector, it should be copied, and the copy stored. If cinematograph films are to be projected frequently, they *must be stored so that they do not shrink to* an extent which would cause damage when run through the apparatus. Acetate films should in these circumstances be stored at a moderate relative humidity, 50–70%, and at a temperature not higher than 70°F. Certain colour films show a tendency for the colours to fade unless the humidity is kept low. Nitrate films to be used frequently should be stored at low temperature and low relative humidity. Film containers for nitrate film should not be *tightly sealed, and the drawers or cabinets* should be vented to permit escape of the gaseous products of decomposition.

The fire hazard present in nitrate film requires special attention in designing storage places. Standards for this have been established by the responsible authorities in many countries and must be adhered to. In general, however, the film is stored in approved cabinets in vaults of fireproof construction, and the cabinets are so arranged that the films are properly isolated so that only the minimum amount is destroyed in case of fire. The system is employed at the National Archives at Washington, D.C., the films being kept in cabinets with metal lined, insulated, individual film compartments, in *such a manner that complete burning of a roll* of film in one compartment should not cause ignition of film in other compartments of the cabinet.

Tests made at the U.S. Bureau of Standards, using accelerated oven ageing, indicated that the chemical stability of commercial acetate films is greater than that of papers of maximum purity for permanent records. The Bureau reports the advisability of preserving negatives of permanent value by making them on acetate *base film. The handling and projection of* cinematograph film in theatres is subject to local regulations. In addition to precautions to guard against fire, the film should be so handled that it does not accumulate dirt and scratches which would affect the quality of the projected picture and the mechanical properties of the film. The conditions of running in the projector should be so adjusted as to prevent tearing of the perforations and other damage.

Types of Films.—The number of different types of photographic film manufactured approaches 100 when considered from the point of view of the emulsion. Considering varieties of film base, special coatings additional to the emulsion, etc., the number approaches 400 as *closely as can be judged. Films are usually* available, or made specially, for all purposes where their use is desirable, limits being provided by the width of the base as made, and the possibility of making emulsions and base having the desired characteristics. A selection of films in common use can be grouped according to their purpose as follows:

Cinematograph films: standard, 35 mm., negative and positive; substandard, 16, *9.5, and 8 mm., reversal, negative, and* positive; special films for sound recording, duplicating, colour photography, copying documents, titles, background positives, etc.

Amateur films: roll films, film packs, cut *film, special films for miniature cameras,* colour films.

Commercial and professional films: usually cut films, for portraiture, press photography, general commercial work, copying, separation negatives for colour photography, special films giving direct transparencies in colour, duplicating film, positive film for transparencies.

X-ray films: cut films for general and dental radiography, usually coated with emulsion on both sides.

Photo-engraving films: cut films for colour separation negatives, continuous tone negatives and positives, screen negatives and positives, stripping film.

Aero films: in rolls for use in aërial cameras, often on low shrinkage support.

Special films: for recording scientific instruments such as oscillographs, electrocardiographs, spectrographs, etc., automatic cameras, documentary photography, picture transmission by electrical methods, infrared photography, sensitised tracing cloth, direct positive paper, etc.

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CELLULOSE.—*Cellulose* is the carbohydrate that is the essential and characteristic structural substance of the plant world: it seems to be present in approximately every part of the plant and, probably, of all plants. Not only is cellulose present in the more elongated fibrous cells, which are further commonly aggregated into lengthier filaments that are the usual interest of the industrialist, but also it is present in the thin-walled, succulent or pithy, more or less round cells, with juicy *contents, that are the food materials of herbivora* and other animal species.

Fibrous cells vary in length from 2 or 3 mm., as in the "paper-makers' fibre'" derived, for example, from wood and esparto, to as much as 20 mm. and more in the cotton staple, ramie, and other cellulose species, sometimes called noble celluloses. Fibre is thereby defined as an isolated, single, elongated cell; filament is, then, a lengthy aggregate of fibres.

Broadly, the older parts of the plant contain the higher percentages of cellulose. In the animal world, also, cellulose is found in the skeletal material of the tunicates; it appears to be present, also, in some bacteria. Whatever its origin, whether plant or animal, cellulose is the same substance chemically.

The chemical composition of cellulose is based on that of dextrose and cellobiose. When cellulose is hydrolysed with dilute sulphuric acid it yields dextrose, and G. W. Monier Williams (J.C.S. 1921, **119**, 803) thus obtained a yield of 90% dextrose. The elementary composition of cellulose is C 44·4, H 6·2, O 49·4, whence the empirical composition $C_6H_{10}O_5$. *Cellulose is to be regarded as the substance composing the walls of the cells in which the reserve material (starch) of the plant is stored.* In order to prevent the cell walls from being attacked by the enzyme used by the plant to break down the starch, cellulose is based on β-glucose, whilst starch is composed of α-glucose. The enzyme key in Emil Fischer's sense will therefore "unlock" starch but not cellulose.

The cellobiose molecule is $(C_6H_{10}O_5)_2,H_2O$, and it is customary to represent the cellulose molecule as $(C_6H_{10}O_5)_n$, where n is now no more than a statistical average, which may be 100 or 200 or more. Formerly, it was usually assumed, conjecturally, to be some small number like 3 or 4 and, then, numerous ingenious structural formulae were also inferred or devised to fit the assumptions, with little valid supporting evidence: it was of no more than historic interest. These older ideas were rooted in what was supposed to be classical molecular theory, derived from the study of gases and, by analogy, true solutions, which assumes a characteristic mean free path, as defined in terms of gas or osmotic pressure; in the solid state, however, that part of the concept fails, the true applicability of theory is thereby impeded and, therefore, other ideas are now found to be more useful.

Micelles and Crystallites.—The micelle (Nägeli, 1858) is conjectured to be the ultimate unit of cellulose structure in the fibre or cell of the plant and the necessity for it, as a conjecture, is based on such studies as those, notably, of H. Ambronn (Kolloid-Z. 1917, 20, 184) and his co-workers on the double refraction of fibrous substances generally, which establish the certainty that they are crystalline in the sense of having an ordered structure, something like brickwork, and especially under stretch which inevitably increases tightness of packing. The micelle is defined as the structural unit of this ordering and to that extent these materials are crystalline; thus, also, the word crystallite has come into use and it is assumed to consist of one or more micelles. In ramie, micelles or crystallites appear to be ordered parallel to the fibre axis; in cotton, screw-wise; other arrangements are possible and evidence thereof is being gradually accumulated.

Dextrose and Cellobiose.—The basis of cellulose structure is the constitutional formulæ of dextrose and cellobiose, which have now been established in all essentials, especially as a result of the labours of Irvine, Haworth and Hirst. Haworth's formula for cellobiose is β-glucosido-glucopyranose (Fig. 1) (maltose being the α-isomer):

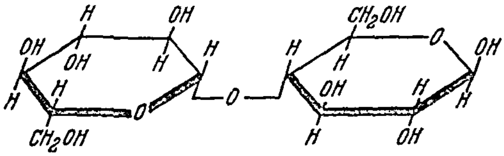


Fig. 1.

With this formula of cellobiose as starting point and on the assumption that the atomic dimensions of carbon, oxygen, and hydrogen are those found by W. H. and W. L. Bragg by X-ray analysis of such substances as graphite, calcium carbonate, and so on, and after earlier preparatory attempts by Sponsler and Dore, K. H. Meyer and others, H. Mark has finally, consolidated and reconciled, in main essentials, all the evidence available, in his interpretation of the X-ray analyses of cellobiose and cellulose as shown in Figs. 2 and 3 (from Mark's "Physik und Chemie der Cellulose": Julius Springer, Berlin, by permission):

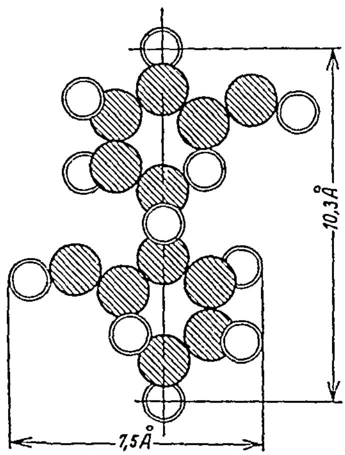


Fig. 2.

As is customary, the hydrogen atoms are omitted in these diagrams.

The dimensions of the unit cell of cellulose are $a=8{\cdot}35$ Å., $b=10{\cdot}3$Å., $c=7{\cdot}9$Å., $\beta=84°$. The diagram also shows that there is one cellobiose unit in the central axis of the unit cell and one-quarter of a cellobiose unit at each of the four vertical margins of the unit cell—the remaining three-quarters of a unit belonging, of course, to the like three contiguous, neighbouring cells at each vertical margin. Therefore, the cellulose content of the unit cell is, arithmetically, $4C_6H_{10}O_5$; and hence, since its weight in terms

of the weight of the hydrogen atom is known and the volume, in Å. units, of the unit cell is easily calculable, the true specific gravity for cellulose is likewise derived arithmetically and found to be 1·55, which agrees perfectly with the precision determination, by direct displacement in helium, due to G. F. Davidson, 1·55–1·57 (Shirley Institute Memoirs, 1926, 4, 41).

According to this evidence, cellulose consists of micelles and crystallites, each micelle being a bundle of parallel chains of dextrose residues (Fig 4, in which the oxygen atoms are shaded); each chain is of variable length and the number of chains in the bundle also variable. The dextrose residues, in each chain, are held together by primary valencies; the chains adhere to one another, in the bundle, by secondary forces; the average micelle size and chain length is like fibre length no more than a statistical average. On this basis and *mutatis mutandis* it may be quite properly argued that cellulose, being made

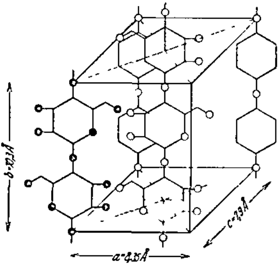


Fig 3.

up of chains of variable length, each of which might be called a molecule, is analogous to a mixture of homologues, such as, for example, purified mineral oil. All experience is consistent with the belief that high quality in cellulose is correlated with high average micelle size and/or chain length, and what is always designated loosely as "degradation" is correlated with diminution of the average, accompanied by the production of detritus products containing substances often oxidised, of far smaller unit size, often approximating to small molecular dimensions and therefore capable of passing into true solution.

Micelle and Chain Dimensions.—There is much that is not very clearly determined as yet of the inter-relations between crystallite, micelle, and chain dimensions, in the above paragraph the word bundle has been added, no more than descriptively; much remains to be done before these words can be used with precision. Something has been achieved, however, and it is feasible to determine some of their dimensions approximately. Thus it is theoretically feasible to calculate the approximate dimensions of micelles or crystallites from the breadth of the diffraction lines in the X-ray spectrogram, but it is difficult to measure that breadth with precision. H. Jancke (1925) obtained values of 112×10^{-8} and 66×10^{-8} cm. for two dimensions; R. O. Herzog and Krüger (1926) similarly obtained a value which they express as a minimum of 20,000 times the weight of an atom of hydrogen. Other methods, based on viscosity, on osmotic pressure, and on

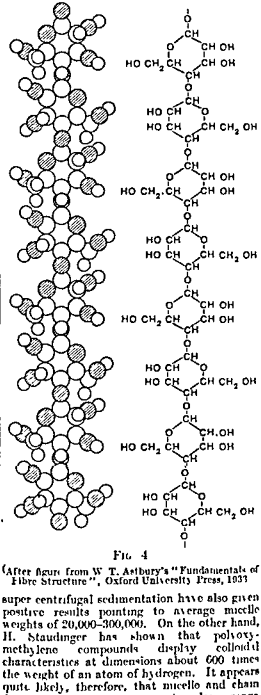


Fig 4

(After figure from W. T. Astbury's "Fundamentals of Fibre Structure", Oxford University Press, 1933

super centrifugal sedimentation have also given positive results pointing to average micelle weights of 20,000–300,000. On the other hand, H. Staudinger has shown that polyoxymethylene compounds display colloidal characteristics at dimensions about 600 times the weight of an atom of hydrogen. It appears quite likely, therefore, that micelle and chain dimensions may vary over quite a large range and still display the characteristic qualities of cellulose over the whole range. Latterly, interest has been awakened in direct determina-

tion of the chain length by taking advantage of the circumstance that the two dextrose residues, at the two ends of each chain, should be capable of substitution by four methyl groups compared with three for each of the intermediate dextrose residues. Haworth and Machemer (J.C.S. 1932, 2270), by direct hydrolysis, obtained 0·6% of tetramethyl glucose from 200 g. of methylated cellulose, from which they calculate an average lower limit, in their material, of 20,000–40,000 as the weight of the chain; they conclude that the chains terminate at a lower mean length of 100–200 dextrose units and that the colloidal properties and organised structure of cellulose are fully explicable from this conception.

Dispersions.—The methods of viscosity, osmotic pressure, and super-centrifuging, just mentioned, relate to dispersions of cellulose; the method of Haworth and Machemer to a dispersion of the trimethyl and tetramethyl cellulose. Such dispersions of cellulose and its derivatives, following much earlier practice, are perhaps still most frequently designated cellulose solutions, and most probably the particles present are predominantly separate chains rather than larger units, *i.e.* bundles or micelles, at all events at low concentrations. Units larger than single chains also persist in these dispersions, to a greater or lesser extent, depending on circumstances. Measurements based on viscosity, osmotic pressure, and sedimentation have yielded rich results when scrutinised on the basis of theoretical developments, originated by G. B. Jeffery (Proc. Roy. Soc. 1922, **102**, 161), as an extension of A. Einstein's law of viscosity for spheres (Ann. Physik, 1906, **19**, 289), to ellipsoids of rotation which may be approximated, geometrically, to chain form for the purposes required. H. Staudinger (Kolloid-Z. 1930, **53**, 19) and his co-workers' investigations showed that viscosities are consistently higher than predicted by theory; reconciliation has more recently ensued (R. Eisenschitz, Z. physikal. Chem. 1931, A, **158**, 78) and it now appears certain that the chain is the ultimate dispersion unit. The word solution would be, to that extent, properly applicable; simultaneously, however, the chains are highly solvated and display all the usual colloid phenomena characteristic of emulsoids; on that basis the word dispersion may properly be preferred.

Cellulose itself is easily dispersed by numerous aqueous reagents; cellulose derivatives, esters, and ethers are dispersed by numerous organic solvents and mixtures thereof; all are highly solvated. P. P. von Weimarn who has devoted many years of investigation to the problem of systematising the phenomena (Kolloid-Z. 1912, **11**, 41; 1925, Festschrift, 106; 1927, **42**, 43), concludes that all easily soluble electrolytes are adsorbed and solvated water (or other solvent) therewith; when the quantities thus taken up in favourable circumstances suffice, the cohesion of the cellulose is overcome by the tensions thus arising and dispersion ensues. Both positive and negative ions are effective additively. R. O. Herzog and Beck (Z. physiol. Chem. 1920, **111**, 291) and especially H. E. Williams (J.S.C.I. 1921, **40**, 221) have assembled data on the basis of the hydration of ions, in ascending order of effectiveness, as follows:

$$NH_4 < K < Na < Li;\ Ba < Sr < Ca;$$
$$\tfrac{1}{2}SO_4 < Cl < Br < J < CNS.$$

Calcium thiocyanate is thus very effective as a dispersing agent because it has a very high solubility, both its ions are greatly adsorbed and both greatly solvated. Earlier and better known dispersing agents (non-neutral, however) are especially zinc chloride (T. Taylor, 1859; Wynne and Powell, 1884), cuprammonium hydroxide (E. Schweizer, 1857) and sodium xanthate, which is the viscose forming reagent, *in situ* (C. F. Cross, E. J. Bevan, and C. Beadle, 1893). On dilution, cellulose is reprecipitated from dispersions in a swollen gelatinous condition, and J. R. Katz (Kolloid-Beih. 1917, **9**, 1) has shown that the phenomena are those of imbibition, commonly named "hydration" among cellulose specialists. He and H. Mark (Z. physikal. Chem. 1925, **115**, 338) have shown also that throughout the changes accompanying adsorption, dispersion, and reversion, by reprecipitation, in neutral media, the X-ray diagram remains that of cellulose alone and there is no evidence in favour of any chemical reaction.

Strong acids, like highly concentrated HCl, disperse cellulose in the cold almost instantaneously—approximately in proportion to their ionization; hydrolysis is very rapid and oxidation likewise, more especially with oxidising acids like chromic acid. At lower acid concentration hydrocelluloses are formed which are disintegrated fibrous residues more reactive to alkalis and characterised by free aldehyde groups; soluble dextrinous substances and dextrose are formed simultaneously. At intermediate concentrations imbibition and gelatinisation phenomena predominate without dispersion; sulphuric acid (sp.gr. 1·5–1·6) applied to paper, for a few seconds, and thereafter quickly washed out is the reagent for the industrial production of vegetable parchment. Salts such as $SbCl_3$, $HgCl_2$, HgI_2+KI, $BiCl_3$, $SnCl_2$, $CoCl_2$, etc., in concentrated hydrochloric acid solution also disperse cellulose rapidly with hydrolysis and, in general, with the same train of phenomena (H. G. Deming, J. Amer. Chem. Soc. 1911, **33**, 1515); under controlled conditions they gelatinise cellulose, and $ZnCl_2$ (70° Bé at 40°) is, thus, much used for the industrial production of vulcanised fibre.

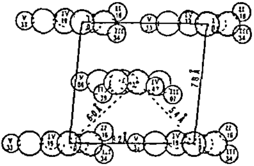
Mutatis mutandis, dispersions of cellulose esters and ethers in organic solvents display analogous phenomena of gelatinisation, dispersion, and reprecipitation. They are of great importance in industry, and many of them are of especial interest, *e.g.* guncotton in nitroglycerin (*cordite*).

Hydration.—There is, thus, a series of interrelated phenomena, adsorption, gelatinization, reversion by reprecipitation; reverted cellulose is always "hydrated." Alkalis react to display all these phenomena, short of complete dispersion.

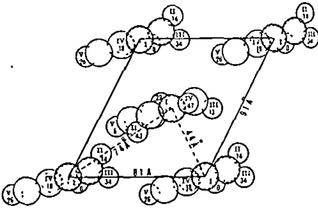
Alkaline hydroxides and alkalis generally have little action on cellulose at low concentrations even when the temperature is raised. At higher concentrations, *e.g.* 12% $NaOH$

and upwards, mercerisation begins (J. Mercer, 1844; H. A. Lowe, 1890); at higher concentrations and temperatures the cellulose is partly dispersed. But even at 180° resolution and dispersion are still limited and gelatinous products are precipitated on dilution; at yet higher temperatures (250°) the cellulose is completely resolved to give acid products of low molecular weights, chiefly acetic and oxalic acids.

Strong alkalis, including alkyl ammonium bases, are strongly adsorbed by cellulose. Up to 12% $NaOH$ the approximate amount adsorbed increases proportionally to the concentration; at 12–25% the amount remains constant, then rises again, and at 34% becomes constant once more. It is now generally agreed that a compound, $2C_6H_{10}O_5\ NaOH$, is formed, especially since X-ray analysis has shown that sodium enters the chain (K. Hess and C. Trogus, Z. Physikal. Chem. 1931, 11, 389). Similar results are obtained with KOH and $LiOH$, $NaOH$ is intermediate between them in accordance with the analogous effectiveness of their salts, cited above. Fibrous cellulose, thus treated with mercerising soda (17·8% weight/weight), undergoes structural modification; it shrinks and it gelatinises, gradually and progressively; when the shrinkage is prevented (H. A. Lowe, 1890) it becomes smooth, lustrous, and even silky. Some of the cellulose substance is dissolved and an important assay method is dependent thereon. Thus, a pulp treated with mercerising solution for 30 minutes at 20°, then diluted and filtered, will give a residue of resistant cellulose, α-cellulose, and the filtrate will contain a proportion precipitable by dilute acetic acid, β cellulose, and a proportion unprecipitable, determined by difference, γ cellulose. Industrially, a high α cellulose content is evidence of high quality because experience has shown that severe previous process treatments, with reagents at high concentrations and temperatures, invariably lower the α percentage, whereas with cautious treatment wood pulps can be made of about 90% α content without undue difficulty; cotton pulps, similarly, have higher percentages. Industrially, α cellulose is



Unhydrated.
FIG. 5.



Hydrated.
FIG. 6.

(From Mark's "Physik und Chemie der Cellulose" · Springer, Berlin, 1932.)

thus identified with undegraded, *i.e.* resistant, cellulose.

In various ways, therefore, by the action of acids, alkalis, and salt solutions, and by reprecipitation, *cellulose undergoes hydration*. The result is obtained the more easily if, simultaneously, mechanical action is applied; in that event, water alone will hydrate cellulose, *and this is an industrial operation* of very great importance in the making of paper. A machine called "beater" or hollander is employed; the purified fibres with water are circulated in an *endless channel*, at one point of which they are forced between bars on the periphery of a drum, rotating in the channel, and other bars on the bed of the channel; they are thus squeezed and rubbed and become a swollen, fibrillated, and cohesive pulp. This allows a sheet of paper to be made that will have adequate strength and other qualities desired. *By* ancient paper-makers, in China, Arabia, and in Europe until about 1700, primitive methods of the "pestle and mortar" type were employed for the purpose.

Cellulose regenerated from its derivatives, *e.g. by saponification of esters, is likewise* obtained hydrated.

Hydrated cellulose, by whatever method obtained, has an X-ray diagram of its own (*Fig.* 6), *differing from that of cellulose itself* (Fig. 5), especially in having an angle $\beta=62°$ instead of 84°; the identity period remains 10·3Å, as for cellulose itself; and that is interpreted as indicating *that hydration produces no* shortening of the chain but only a vertical twisting; the dimensions and diagrams (bird's eye) display the nature of the change:

Cellulose: $a=8{\cdot}35$Å., $b=10{\cdot}3$Å., $c=7{\cdot}9$Å., $\beta=84°$.
Hydrated Cellulose: $a=8{\cdot}14$Å., $b=10{\cdot}3$Å., $c=9{\cdot}1$Å., $\beta=62°$.

Whenever, by loss of water, hydrated cellulose reverts to unhydrated cellulose, the unit-cell dimensions revert simultaneously. The well-known twisting and tightening produced *by* mercerising is easily visualised on this conception. The specific gravity of hydrated cellulose is about 1·52 and, therefore, as before, there must be, arithmetically, four dextrose *residues in*

the unit cell, which is again understandable. The hydration water entering the cellulose does not enter the unit cell and is therefore not inter-chain but inter-micellar water; it is imbibition water and not chemically combined. This last inference is in accord with J. R. Katz' work (*l.c.*), which established that the laws of imbibition apply to the inter-relations between water and cellulose. J. Strachan (Proc. Technical Sect. Papermakers' Assn., 1926, VI, 160; *ibid.* XII) has applied this knowledge to the action of the hollander during beating. On the other hand, it has been argued (C. J. J. Fox, *ibid.* 1926, VI, 170; 1932, XIII, 1) that a chemical hydrate is still a possibility, though it would be manifestly difficult to identify its separate presence in contact with the large excess of imbibition and loose surplus water simultaneously present. Nevertheless, H. Mark (World's Paper Trade Review, Technical Convention, March 1933, 70) produced new experimental evidence, based on direct measurements, of adsorption of water by cellulose, at such low pressures as 1 mm., that water does enter the chain and may, therefore, be regarded as in chemical combination. The molecular equivalent of water is small by comparison with a dextrose unit and the weight of it thus concerned is likewise small by comparison with imbibition water.

Cellulose is in reversible equilibrium with water vapour over the whole range of humidities and temperatures occurring in the atmosphere. The reversibility is accompanied by hysteresis, analogous to what is found generally true for solid substances, and is dependent upon surface condition, and therefore previous history, and other variable factors. An elaborate study of cellulose-humidity relationships has been made by A. R. Urquhart and A. M. Williams (J. Text. Inst. 1924, **41**, 130). Cellulose ordinarily contains atmospheric moisture with a minimum of about 5%. For many industrial purposes conditioning by storage in constant humidity rooms is required as an antecedent preparation; it is therefore standard practice to calculate all analytical data on oven-dry weights, obtained by heating to constant weight at 100°–105°.

Industry.—The multitudinous utilisations of cellulose remind us that ours is a cellulose age as much as it is an iron or steel age. The cellulose is derived from a great variety of plant raw materials, and by a great variety of methods. Cotton, the buoyant seed hair of *gossypium*, is purified almost solely by mechanical devices (ginning) which effect the removal of seed, dirt, etc., and thereafter a simple cleansing treatment, including bleaching, suffices to give it the whiteness that is usually desired; the mildest laundry reagents, dilute soda ash, bleach, and soap are employed for the purpose. Bast fibres, which include flax, hemp, ramie, jute, sunn-hemp, and the vascular bundles of leaf fibres such as manilla, sisal, phormium, are freed from woody, cuticular and thin-walled, fleshy cells by which they are accompanied in the living plant. This is effected by digesting in water, whereby enzyme and bacterial fermentations of the pectinous, sugar and starchy matters present are induced, which loosen and free the cellulose filaments; thereafter, mechanical treatments (scutching, heckling, beetling, etc.) suffice for most industrial requirements for which they are employed. Fatty, waxy, and ligneous non-cellulose residues, ingredients and incrustants still remain in the fibre and for many industrial purposes they are not disadvantageous, and such fibres are invariably used without further purification. But they can be further purified, if desired, by treatment with alkali and bleach or by more drastic removal of non-cellulose; ordinarily they encounter such treatments only when they appear at the paper mill classed as "rag" to be made into paper.

Pulp.—The vast output of purified wood cellulose, for paper industries, is obtained by direct chemical attack for the removal of the non-cellulose components and incrustants of cellulose, amounting to about half the wood substance; they are waxes and fats, terpenes, resins, tannins, gums, pectins, sugars, starches, and especially lignin, which adheres to the cellulose as incrustant. Autoclave digesters of large size, frequently taking 50 tons and more of wood chips at a charge, are employed. Calcium bisulphite is the reagent most in use (B. C. Tilghmann, 1866; C. D. Ekman, 1874). This "bisulphite pulp" is made, either at lower concentrations and lower temperatures (2·5–4·0% SO_2; 110°–125°) to give "strong" or "Mitscherlich" pulps, which are not very easy bleaching and are much employed unbleached as a component (about 20%) of modern newsprint (about 80% ground-wood being the other component), or it is made at higher concentrations and temperatures (4–5% SO_2; 125°–140°) to give Ritter-Kellner "easy bleaching" pulps, which are the commonest ingredient of modern white papers. Half the wood substance and all the calcium bisulphite are a trade waste and total loss, for which there is, at present, no appreciable industrial utilisation; it is the largest single item of trade waste in the world to-day, amounting to many millions of tons yearly. Calcium ligninsulphonate is its principal ingredient, but fermentable sugars, starches, tannins, etc., are also present from which alcohol is to a very small extent recovered and other utilisations (*e.g.* tanning) are of negligible dimensions. The cheapness of limestone and of SO_2 from pyrites burners accounts for the economic success of the process, in spite of the loss of about half the wood substance. A more serious practical restriction is that this reagent, being acidic, is not very effective in removing resins, which are not very soluble in acids; hence, the least resinous woods have to be employed, especially spruce. Bisulphite pulps, prepared to customary requirements of the trade, are the raw material of the great viscose industry, which produces, at no great cost above that of paper pulps, about 90% of the world output of rayon, these pulps have about 90% α-cellulose, low ash (0·1%), low resin residue (0·5%) and suitable swelling quality (in mercerising soda).

The resinous woods (firs, etc.) require an alkaline digestion; the sodium sulphate in the reagent used becomes transformed into sodium sulphide,

accompanied by production of substances allied to mercaptan. It is owing to this fact and to the consequent unpleasant odours produced that the manufacture of the pulp has to be carried out in sparsely populated districts. The reagent is recovered at the end of the digestion, by evaporation and incineration, and then recuperated with additional sulphate or with caustic soda and used again as an essential economic necessity. The pulps thus obtained are employed especially for making the very strong "Kraft" papers now so much used as wrapping, the great strength is related to the mildness and reducing action of the reagent and its consequent inhibition of oxidation of the cellulose. These pulps are not easy bleaching and were never bleached until the recent present-day cheapness of chlorine brought also bleached "Kraft" into the market.

Esparto (T. Routledge, 1856) is much used in Great Britain, especially Scotch mills, and little elsewhere, as a paper fibre. Esparto grass imported from Mediterranean areas is invariably pulped at the paper mill by the use of caustic soda exclusively, the caustic soda is recovered by evaporation and incineration, and then recuperated by lime and used again.

Straw is much used, boiled with lime for cheapness, for the manufacture of straw-board. In S America, S. Africa, and elsewhere, where there are local supplies available, straw is now coming into increasing use also for the manufacture of white papers for local markets.

ANALYSIS.—For all these grades of cellulose, of various origins and prepared by many processings, there is now much accumulated experience available for their assay, in general these methods have been developed, *ad hoc*, on the basis of industrial needs and empirical observations. The following methods cover all but quite exceptional requirements.

For purposes of comparison, "standard cellulose" is taken as datum; it is generally prepared from ginned cotton by heating first with 0 1% medical soap solution, thereafter well washed and heated with 0 5% Na_2CO_3 solution, washed, then heated with 0 1% NaOH solution, drenched with cold distilled water, immersed in NaClO solution (0 1% Cl) for one hour, filtered off, and washed until free of Cl It may still contain a minute trace of fat and wax from which it may be freed by extraction with alcohol benzene. For many purposes quantitative filter papers may be used; the HCl and HF extractions to which they have been submitted make them, however, rather more reactive than standard cellulose, in consequence of minute traces of hydrolysis products; the same is true of medical cotton, which is frequently used.

The cellulose content of a raw material is determined by chlorination (Cross and Bevan, 1880). Preferably, the material is first extracted with alcohol-benzene for removal of fats and waxes, then washed with hot water and squeezed, then heated with 10–15 parts of 1% NaOH solution for ½–1 hour at constant volume. It is then squeezed and, still moist, submitted to the action of a regulated current of chlorine gas for 1 hour. Surplus chlorine is removed and the material then covered with a known volume of distilled water, an aliquot portion of which is titrated for HCl, the reaction being partly substitution and partly addition, and the HCl figure thus obtained is a useful indication of the amount of lignin present in the material. After washing free of acid, the material is placed in a 2% $NaSO_3$ solution and gently raised to the boil, 0 1% NaOH on the weight of the solution is then added and the purified fibre finally washed with water just acidified with acetic acid, filtered off, dried, and weighed. The yield obtained includes fibrous and non-fibrous cellulose; it often contains also pentosan derivatives (xylan and araban derivates, mostly), for which a correction may be required and the degradation products of hydrolysis and oxidation may also be present. It is routine practice to distil the fibrous yield, therefore, with 10–12% HCl and the furfural thereby produced is then determined by precipitation with phloroglucin, a standardised empirical procedure being followed, otherwise reproducibility will be unsatisfactory.

This chlorination method gives, in effect, a maximum value which may very well be a higher yield than is likely to be attained in industry, with its processing methods based on higher concentrations and temperatures and causing greater losses in consequence of hydrolysis and oxidation; but though a great many other methods of assay have been suggested from time to time with varying success it has survived supreme, throughout the world, as the most dependable and useful method known.

The material sometimes, though rarely, has to be chlorinated a second time if it is of a hard and highly lignified nature; alternatively, the preliminary alkaline treatment may be intensified. The final product, if coloured, may be treated with very dilute (0 05%) bleach or permanganate and thereafter washed with water acidulated with SO_2, washed, dried, and weighed. It is then invariably in the condition of ultimate fibres and their length is given as a simple average, either by direct measurement in a microscopic field or by casting the image thereof on to a screen and measuring a number of the magnified screen images with a foot rule. The following are representative dimensions of a few commonly occurring fibres:

Cotton	Average length, mm.	Diameter, mm
Cotton . .	20–40	·012–·035
Hemp . . .	15–20	·015–·050
Ramie	50–200	·030–·075
Flax .	20–30	·015–·040
Jute . . .	1·5–4	·020–·025
Sisal . . .	1·5–6	·015–·028
Phormium .	5–15	·010–·025
Esparto . .	0 5–3	·010–·020

The yield and average fibre length, together with the pentosan content having been determined, the following tests may then be required. Ash content, quantitative, and sometimes

qualitative, is important in, for example, viscose pulps because the minute orifices of the spinnerets may be stopped by mineral impurities; in some cordage siliceous ash may suggest fibre damage by cutting; finally, in quantitative filter papers ash content is of well-known importance. Ash content is determined by burning off the cellulose and weighing the residue. The loss suffered by boiling with 1% soda for (*a*) 5 minutes, (*b*) 1 hour, is a measure of hemi-celluloses, and the determination of "copper number" (Schwalbe, 1907) by the modification of Braidy's method devised by Clibbens and Geake (Shirley Inst. Memoirs, 1923, 238) is a more specific measurement for the same purpose, now much used. They employ sodium carbonate instead of the hydroxide in the Fehling's solution, with practical advantages of reproducibility.

Lignin is present in the great majority of cellulose materials, either in original percentage or as surviving residue. Qualitatively, lignin may be isolated, though not unchanged, by dissolving away the cellulose accompanying it with highly concentrated HCl and then washing and filtering off the lignin; 72% H_2SO_4 may likewise be employed. Many investigators have also used these methods more or less quantitatively but there is no uniform, agreed standardisation that gives adequate reproducibility. Ground-wood, which, of course, contains the full original content of lignin of the wood, frequently has to be determined (*e.g.* for assessment of customs import duty, in some countries) and an empirical method of determining the lignin as a measure of the ground-wood content of paper, has been systematised by H. B. Dunnicliffe and H. D. Suri (Analyst, 1932, 57, 354); based on interaction of lignin and phloroglucin, with specified procedure, it gives adequate reproducibility.

Finally, and especially, determinations of α, β, γ-cellulose content and cuprammonium viscosity will often be required. Cuprammonium hydroxide solution (Schweizer reagent) has long been known as a good dispersion agent of cellulose and, in use, for the production of rayon, though the viscose method has greatly outgrown it, and for the production of Willesden canvas and paper; the viscosity of its dispersions has been, in recent years, much employed as a measure of quality in the sense that longer chains give higher viscosities than shorter ones in accord with theory (*see* above). In this dispersion the cellulose appears to undergo no degradation for perhaps a week and more, when excluded from oxidation by the air. The standard specification of the Fabrics Research Committee (D.S.I.R.), H.M. Stationery Office, 1932, details the method; cellulose concentrations of 0·5–2·0% are commonly employed; the lower the degradation of the cellulose and the greater the average fibre length the higher will be the viscosity. This determination considered together with the "copper number" and other data will provide much information about history and quality, without which the high systematisation now attained in, for example, the rayon and lacquer industries would have been impossible.

DERIVATIVES.—The only derivatives of cellulose for consideration are the esters and the ethers. Theoretically, their number is very large, and the size of two treatises dealing with these derivatives (E. C. Worden, "Technology of Cellulose Esters," Vol. I, i–v, 1921; "Technology of Cellulose Ethers," 5 vols., 1933, Newark, U.S.A.) is eloquent testimony of the number of these compounds that have been already prepared and described. Actually, however, to-day three esters are of paramount importance, namely, the nitrate, the acetate and the xanthate; and none of the ethers has more than academic interest as yet, though their patent literature is already considerable.

Haworth's formula (above) displays the presence of three alcoholic OH groups in each of the dextrose residues of the cellulose chain, except that there are four in each of the residues at the two ends of the chain; each OH can be esterified or etherified:

$$R'-OH+R-COOH \rightarrow R'-COOR+H_2O$$
$$R'-ONa+RX \rightarrow R'-OR+NaX$$

Theoretically, therefore, since there are three alcoholic OH groups available, mono-, di-, and tri-esters and ethers are possible. Actually, however, X-ray analytical studies of the problem have established that when cellulose is progressively nitrated the spectral diagram begins as that of pure cellulose and continuously fades and merges into a new one without discontinuous halts. The same thing occurs in all the other esterifying and etherifying processings that have been studied, and the interpretation of these facts, consistent with diffraction theory on which the reasoning is based, seems to be that when a molecule of reagent interacts with an OH it does so at random until all OH's have thus been esterified or etherified. In this sense there is no homogeneous mono- or di-substitution product, but hybrid-like, part-cellulose, part-ester or ether products. The xanthate ester is altogether singular and exceptional in that only a mono-substitution product occurs; many early attempts were made to obtain di- and tri-substitution production without success.

Nitrocellulose.—The nitration of cellulose (Schönbein, 1845) has long been a fundamental process in the explosives industry, and principles and practice are derived therefrom. At concentrations up to 75% HNO_3, nitric acid has an effect on cellulose in the sense that there is a gradual change of the X-ray spectrogram analogous to hydration and the hydration diagram appears on dilution with water; above 75% the true ester diagram begins to emerge. No approximation to completion of the esterification occurs, however, unless H_2SO_4 is employed simultaneously, in accord with the usual practice. The complete esterification corresponds theoretically with a final content of 14·14% of nitrogen; the theoretical percentage has, however, *never yet been attained* and 14% must be regarded as the maximum practically attainable.

Broadly, the procedure adopted is as follows. Cotton linters are the raw material; they are the shorter seed hairs, amounting to about 15%,

which are removed from the longer hairs, in the operation of ginning, as being not suitable for spinning. The linters are cleaned and lightly bleached to a specification. Other celluloss containing minute traces of hemi celluloses and pentosans are, of course, very easily esterified. These yield products of low uniformity and stability involving complicated and possibly unsolvable problems of ballistics, storage, and safety; nevertheless, it is a frequently recurring rumour that wood cellulose can be and has been used as a satisfactory substitute for cotton by beleaguered nations in war; there is no evidence warranting these rumours and much evidence that ought to discount them.

The detail of the nitration proper is variable and modified to suit the special requirements of utilisation, which will be different, *e g* for explosives and for lacquers, etc, $H_2SO_4/HNO_3 = 3/1$ with 1–2% H_2O and linters/acid mixture $=1/150$ at temperature 15°–18° for 7 hours is a representative prescription. Evenness of wetting is of the highest importance and therefore the linters are added to the acid mixture in small portions with good mixing At the end of the nitration the mix is cooled to 0° and after squeezing out the surplus acid the material is vigorously stirred into 50% acetic acid, the temperature being kept below 10°, thereafter squeezed off and treated with fresh 50% acetic acid, brought to the boil for 1 hour and then similarly treated with alcohol, which removes the last traces of sulphuric acid After drying in high vacuum such a product generally contains about 13 75% N.

"Stabilisation" is essential, and this is effected by prolonged and repeated washing and boiling of the pulped nitrocellulose. This method is to some extent an alternative to the above treatment with acetic acid and alcohol, by which it can be greatly shortened, with the advantage that diminution of nitrogen content is minimised. The best solvent for high-nitrogen nitrocelluloses is acetone, and for long it was regarded as the only appropriate solvent; for less highly nitrated products alcohol ether (and other cheaper mixtures, for lacquers) is satisfactory, and was used instead of acetone during the war, when supplies of this solvent were insufficient Most important, nitrocellulose disperses exceptionally well in nitroglycerin for the production of a great range of explosives, including cordite Similarly, it disperses, also exceptionally well, or plasticises with camphor to produce celluloid (*q v*) The ease of dispersion and plasticising accounts for the successful utilisation of nitrocellulose for so many purposes—explosives, lacquers, plastics, for the like reason it was also the first, and for long the only material that could be handled for the manufacture of rayon. Its explosive, combustible and ignitible qualities made it dangerous and so it had to be denitrated and thus reconverted to cellulose. This was done by means of sulphide solution suggested by J. W. Swan (1882), who was a pioneer of nitro silk manufacture. To this day, and in spite of much investigation, no better agent for denitration than sodium or ammonium hydrosulphide is known; it is effective and smooth in action in the sense that it does not cause any degradation of the cellulose, and its effect can be very easily controlled so as to stop at any predetermined point.

The variations of procedure that have to be followed for the production of nitrocellulose have been multiplied by the development of new industries in recent years; thus, lacquers are required containing cheap solvents, and these blended solvents must be "balanced" so that they will evaporate gradually and in succession, giving no super-cooling of surface on which atmospheric dew might deposit and lead to an undesired "bloom." Moreover, the lacquer having all those desirable qualities must have a sufficient nitrocellulose content and possess a sufficiently low viscosity to enable spraying to be employed at appropriately low pressures or, alternatively, flooding procedure may be employed. Industry has succeeded in fulfilling all these obligations, most successfully, by varying the quality of the cellulose raw material, the nitration procedure, and the solvent blending, and by the introduction of many new plasticisers, which are to-day perhaps indistinguishable from high boiling solvents. Steaming cotton linters under controlled conditions enables them to be prepared to provide a nitrocellulose having any specified viscosity over a scale of viscosities graduated from 1 up to 2,000, this remarkable effect of steaming is something for which no understandable explanation, based on theory, is yet available The determination of viscosity by the standardised cuprammonium method has been of decisive importance in achieving these valuable results.

Acetylcellulose.—Schutzenberger (1865) heated cellulose with acetic anhydride and found there was an interaction, Franchimont (1879) introduced the idea of employing a catalyst and he used sulphuric acid and several other substances for the purpose; a large number of substances have since been used and made subject matter of numerous patents, but acetic anhydride in presence of sulphuric acid is the reagent now in use Cotton linters, as for nitrocellulose, is the raw material for the like reason of quality and uniformity, wood cellulose does not yield so useful a product, but the possibility of finding a satisfactory method of employing it is probably more favourable than for nitrocellulose, because difficult problems of ballistics and safety do not arise The maximum acetyl-content for the tri acetate is 62 5 (as AcOH), but 60 is rarely exceeded industrially, and it then disperses slowly in chloroform, which is, however, commercially not a practical solvent. It was not until G W. Miles (U.S.P. 838350, 1906) discovered that controlled hydrolysis (halted at an acetyl content of about 55) provides a product easily dispersible in acetone, that cellulose acetate became a useful industrial product Eventually the war brought it into important use as a safe, non explosive lacquer for aircraft wing fabric, to which it gives a very desirable shrunk water resistant finish (*cf.* B.S.S 2D50); and though very transparent to ultra-violet light, which is potent at high altitudes and destructive

of cellulose, that defect was countered by the use of an added aluminium pigment. Afterwards the industrial plant was converted to the successful manufacture of acetate-rayon, which is now a considerable industry, though far smaller than the viscose-rayon industry. Cellulose acetate is also much employed for plastic moulding, injection moulding especially. It has an exceptionally high dielectric constant which makes it useful in the electrical industry as an insulating lacquer, and it is very transparent to ultra-violet light which makes acetate film useful for some purposes instead of glass. Thin film made from cellulose acetate is also used as a wrapping material and for decorative purposes.

The acetylation operation is not varied to the same extent as that of the nitration, the range of graded requirements being much smaller. A mixture of 120 parts anhydride, 200 parts glacial acetic acid, and 6 parts sulphuric acid is suitable and typical; it is cooled to 5° and the cellulose (air-conditioned to 2–3% moisture content) added in portions with very perfect mixing until the proportion is about 8–10 of mixture to 1 of cellulose; simultaneously the temperature is controlled so that it rises to 10°–13° at the end of about 2 hours. In the next half-hour it will reach 15° and the mass becomes doughy. The temperature, under control, continues to rise gently and is not allowed to exceed 35°. Samples are drawn for routine empirical tests and eventually water is added, which converts surplus anhydride to acetic acid, and the mass is allowed to stand some hours at 50° (until the acetyl number, originally about 60, has sunk to about 55) and by then it has also become acetone soluble, as now required by industrial practice. The recovery of acetic acid and acetone, in this industry, has been developed to a very high level of efficiency, as an indispensable economic necessity. It will be noted that the addition of acetyl groups to the original weight of cellulose is a favourable economic factor.

Xanthate.—More than 85% of the world's output of rayon is made by the viscose process (xanthate). The raw materials are wood pulp, caustic soda, and carbon disulphide; in cheapness it is paramount and recovery is not essential to economic success. The technical difficulties that have had to be overcome have been so enormous that it is evident they would hardly have been so patiently fought if it had not been for these economic attractions.

The wood pulp that is the almost exclusive raw material of this process (cotton is used to a small and probably diminishing extent) is a special but not specially expensive grade, made from spruce, though it is certain that it can be made successfully also from a few other species. A viscose pulp assays approximately 90% α-cellulose, 2–3% β and 7–8% γ, copper number 1–1·5, ash 0·1, resin 0·5, cuprammonium viscosity (1%) about 25 centipoises, and a swelling number about 6 or more (i.e. ratio of mercerising soda taken up to original pulp weight.) The pulp is received in sheets of standard size to fit the steeping tanks employed; it is air-conditioned to a controlled humidity, then immersed for 2 hours in 17·8% $NaOH$ solution in a steeping tank, fitted with compression ram, where it swells greatly; it is then squeezed down to three times the original weight and torn into crumbs to be stored in closed boxes, for 2–3 days at 20°; some oxidation occurs which seems to be a useful and perhaps essential factor in the process. Thereafter carbon disulphide is added (one-third the weight of the original cellulose) so that vapour and not fluid acts on the crumbs, which then gradually swell and become orange-coloured. Surplus carbon disulphide is removed by ventilation and suction and the xanthated crumbs are then dispersed by churning with $NaOH$ solution. At first the viscose dispersion is dough-like; but synæresis occurs on standing and when the viscosity has thus fallen to an appropriate controlled level it is ripe for spinning; that point is decided by determining the quantity of standardised salt solution just sufficient to cause coagulation. From the minute orifices of spinnerets it emerges as fine filaments into a coagulating or setting bath of about 10% H_2SO_4, which neutralises the soda, and coagulates as a consequence. Free sulphur is thus formed in the reverted cellulose and it is easily extracted with Na_2SO_3 aq. Numerous additions to the bath have been from time to time used and patented and some are still employed, *e.g.* glucose, their effect being to modify favourably the cross-section of the fibre, probably by osmotic influence. Alternatively, the viscose may be forced from a narrow slit to form thin film, which is now being used in ever-increasing quantity as an attractive wrapping material and for decoration purposes, often coloured.

The viscose dispersion employed for spinning has a composition of cellulose 7–8%; $NaOH$ 5–6·5%. The reaction is:

$$2C_6H_{10}O_5,NaOH+2CS_2+NaOH \rightarrow 2C_6H_9O_4\cdot O\cdot CSSNa+2H_2O$$

The sulphur content can be determined by adding excess of standard iodine and titrating the excess; another sample of the same viscose is salted out and the sulphur content of the liquid alone is similarly determined; the difference of the two quantities is the quantity of sulphur combined in the cellulose. Further, cellulose xanthate, being the salt of a strong acid, is not decomposed by acetic acid; a double titration with acetic acid and afterwards with sulphuric acid gives values for the free alkali and combined alkali.

This industry had to be developed before much was known about imbibition, solvation, and synæresis; the ripening process was mastered empirically, after endless misadventures. The particles in the dispersion are largely, perhaps predominantly, chains and the condition of the cellulose raw material is probably a master factor in the sense that a high swelling number may mean that many OH groups take up Na atoms and hence become responsive to subsequent attack by the CS_2. However that may be, the disperse particles are certainly highly solvated; the water adsorbed on the particle increases its dimensions and simultaneously diminishes the amount of free

water in the external phase, which is, in effect, *an increase of cellulose concentration* Thus the viscosity is high on account of large dimensions of the particles and on account of the small effective amount of free water, all this is apart from the circumstance that chain length itself gives high viscosity by comparison with spherical particles The disperse phase, sodium cellulose xanthate, is continuously decomposing spontaneously (ripening) and progressive viscosity changes ensue, on that account, which are the basis of the procedure followed in spinning The xanthate ionises, as soap does, to give a negative micelle ion, with imbibition water in its envelope, the *spontaneous decomposition gives free cellulose*, sodium hydroxide, thiocarbonate and water so that the external osmotic pressure rises and abstracts further water from the, as yet, undecomposed and solvated xanthate and thus further reinforces the amount of free water in the external phase, all these effects lower the viscosity Eventually the amount of free cellulose increases to such an extent that the amount of yet remaining undecomposed xanthate, which is a strong protective and emulsifying colloid, becomes insufficient to retain the dispersion and the emulsion breaks; the cellulose coagulates progressively and after a *lengthy period becomes a lump of hydrated* cellulose in a watery fluid (C J. J. Fox, J S C I. 1930, 49, 83T) As this synæresis proceeds a point is reached at which the appointed amount of standardised salt solution will just cause coagulation, and it is thus known that the viscose is of the appropriate ripeness for spinning It will be noticed from the equation that an excess of free NaOH diminishes the rate of the spontaneous decomposition, by mass action, and hence increases the life of the dispersion and the ease of controlling the ripening, and it diminishes the viscosity by increasing the external osmotic pressure, therefore excess *caustic soda is always employed* Actually, it is found that about 7–8% of total soda gives the maximum benefit and more produces salting out effects, in practice, however, the total soda employed is generally 5–6%, because it is found that this gives satisfactory results and consumes, by neutralisation, less acid in the setting bath, as an economic offset These considerations have been of decisive importance in the industry because the pressures required for forcing the viscose through the minute orifices of the spinnerets and through the porcelain (candle) filters employed are considerable.

ETHERS.—Cellulose ethers are as yet of no industrial importance, they are more difficult to prepare than the esters, and especially to ensure minimum degradation of the cellulose, etherifying reagents are relatively costly and the *choice of suitable solvents and their* economic recovery are not yet adequately explored. Nevertheless, it is to be anticipated that their comparative inertness and greater resistance to numerous reagents will qualify them as useful for many purposes, when the outstanding problems have been satisfactorily solved.

The work of T. Purdie and J. C. Irvine (1903) *on the alkylation of sugars prepared the way for* the alkylation of cellulose, and O. Leuchs (1912) and L Lilienfeld (1912) took out early patents for the preparation of cellulose ethers. W. S Denham and H. Woodhouse (J.C.S. 1913, 103, 1733, 1914, 105, 2357, 1921, 119, 81) have made systematic studies of the detail of etherification A description of the preparation and some of the qualities of trimethylcellulose will here suffice, which are, *mutatis mutandis*, typical for other ethers as well. Alkali-cellulose prepared from cotton linters is the raw material; it is torn into crumbs and submitted to the action of the etherifying agent, *which is in this instance dimethyl sulphate*, under pressure at 130° for 8 hours. The reagent must be in copious excess because much of it is saponified by the alkali present and is inoperable in consequence, commonly, the operation has to be repeated with another charge of reagent before a result approaching the theoretical is obtained In this way a methyl content of 43–44 is attained, theory being 45 5 (as OMe) Trimethyl cellulose is soluble in cold water and insoluble in hot water and this curious result seems to be an interesting instance of desolvation with rise of temperature and precipitation as the consequence. Hence the product is purified by *washing with hot water and cold alcohol, in* which it is insoluble Trimethylcellulose dissolves easily in pyridine, chloroform, benzene, glacial acetic acid, ethyl acetate, and many other solvents; it is insoluble in ether and cold alcohol *It can be thrown out of a benzene* solution, as a white powder, by light petroleum, and by slow evaporation it can be crystallised from solution in several solvents, sometimes as spherulites, sometimes as needles.

The triethylcellulose is usually made with ethylchloride as reagent; it is insoluble in cold water, as well as hot, but otherwise its properties are very similar to those of the methyl ether

X ray spectral studies have been made with many of the ester and ether derivatives by K Hess and C Trogus (*l c.*) and they conclude that the introduction of groups into the chain *leads to no alteration of the identity* period, which remains always 10 3Å; but there is a change of the angle so that β 53° for the trinitrate, 93° for the perchlorate; the acetate seems to have two forms and there are anomalies about its cell angle. In every instance, however, only the tri-substitution product is homogeneous

Bacterial Degradation—The usual result of any process attacking cellulose, whether in the laboratory or in the factory or in nature, leads to what is called "degradation," which may be defined as a diminution of chain length and/or micelle dimensions with the formation of *detritus products, frequently oxidised. In* nature such changes are always occurring as a consequence of the processes of living germs and enzymes; these changes are, no doubt, often, and perhaps always, symbiotic. The herbivora ingest cellulose and a bacterial flora in their intestinal tracts converts it into sugars which the beast uses as food; the decay of vegetation

leads to the transformation of cellulose into products such as humus, peat, and coal. There are aerobic, anaerobic, denitrifying, thermophilic, and other bacteria that appear to thrive on cellulose, in favourable circumstances, to yield a variety of products. The study of these processes is rudimentary, as yet, from the circumstances that pure cultures seem to be unattained and cellulose is in nature never unaccompanied by other substances. Hydrogen and methane are almost invariable products, carbon dioxide, formic and acetic acids, and many higher fatty acids, alcohol and lactic acid are commonly formed. H. Pringsheim (Zentr. Bakt. 1909, **23**, 300) suggests that the intermediate production of sugars from cellulose is an cellulose is an essential of the bacterial nitrogen-fixation process.

Compound Celluloses.—In the living plant cellulose is almost always in intimate association with a great variety of other substances. So intimate is this association that it has been customary to designate them "compound celluloses" in the belief that there is chemical combination of the cellulose with them. Plant physiologists for purposes of classification have enumerated (*a*) lignocelluloses, (*b*) cuto- or adipocelluloses, (*c*) pectocelluloses.

Lignocellulose is an aggregate of cellulose so intimately encrusted with lignin that it can be removed only by the drastic attack of reagents as already described. Nevertheless, the X-ray study of lignocelluloses shows invariably that the spectrogram obtained is that of cellulose itself; and the only permissible interpretation of that fact, according with diffraction theory, is that the lignin proper present has not an ordered arrangement, as cellulose has, and hence is unable to display the diffraction spectra that would permit its constitution to be deduced as has been done for cellulose. In lignocelluloses it is therefore an incrustant and nothing more and that diminishes the likelihood of there being a combination. K. Freudenberg (Ber. 1933, **66** [B], 262) has studied the chemical constitution for many years and concludes that there is no combination.

The like reasoning applies to the cuticular or adipocelluloses, which are the characteristic components found in cuticular and cork materials. Fats, waxes, tannins, terpenes, and other substances in great variety can be isolated from them; many of them are in industrial demand, for a variety of purposes, and their study belongs to plant chemistry rather than to the chemistry of cellulose.

The pectocelluloses are associations of cellulose with pectic, often gummy, substances which may be carbohydrates or akin to them; they are often acidic, sensitive to hydrolysis and the action of ferments, yielding pectin, which is present in fruit juices. There appears to be no proper reason for supposing they are chemical compounds of cellulose.

Cellulose in the necessities, amenities, and luxuries of life may be broadly classified as follows:

(1) Food.—The foodstuff of the herbivora is partly cellulose which is converted by their intestinal flora into sugars; hence, indirectly, cellulose is ultimately a source of food for man.

(2) Textiles.—Fine: cotton, flax, etc., for clothing, furnishing, and other fabrics. Coarse: jute, hemp, manila, sisal, etc., for coarse fabrics, wrappings, and cordage. Miscellaneous: straws, canes, coir, bast, kapok, in many arts and crafts.

(3) Pulp and Paper.—From rag, commonly residues from the textile industries; from wood (purified chemical wood and ground wood); esparto, straw for paper and for straw-board.

(4) Constructional.—Timber for building, joinery, cabinet-making; cork and linoleum industries, as adjunct.

(5) Derivatives of cellulose, esters and reverted cellulose:

(*a*) Explosives—nitrocellulose.
(*b*) Lacquers—nitrocellulose; acetylcellulose for aircraft dope.
(*c*) Plastic masses—nitrocellulose for celluloid; acetylcellulose for injection and other moulding.
(*d*) Films—nitrocellulose for photographic and cinema film; acetylcellulose for safety film; tissues—mostly from viscose and some from acetylcellulose.
(*e*) Rayon—85–90% from viscose, remainder is acetylcellulose and cuprammonium rayon.
(*f*) Surface treatments—Willesden canvas and paper, by treatment with cuprammonium hydroxide (Schweizer reagent); vulcanised fibre, similarly with zinc chloride; vegetable parchment similarly with sulphuric acid; military webbing equipment is viscosed.

(6) Decomposition products, miscellaneous.—
(*a*) Bacterial—humus, peat, lignite, coal.
(*b*) Wood distillation products.
(*c*) Oxalic acid.

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C. J. J. F.

CELLULOSE LACQUERS AND CELLULOSE ESTER SOLUTIONS.

The "cellulose" lacquers are solutions of cellulose esters in organic solvents. The ester employed is generally cellulose nitrate (nitrocellulose, nitrocotton, pyroxylin, collodium cotton, collodion cotton) which has been pre-treated so that its

solution has a relatively low viscosity. A typical lacquer contains also varnish gums, natural or synthetic. Solid plasticisers (plastifiers) of nitrocellulose may be present. The liquid ingredients are volatile solvents of nitrocellulose and of the varnish gums, low, medium, and high "boilers" being used, and volatile diluents petroleum or benzene hydrocarbons; alcohol may be classed as a diluent although it acts as an auxiliary solvent for nitrocellulose and as a primary solvent for some of the varnish gums. Mixtures of non-solvents of nitrocellulose may function as solvents, *e g.* alcohol + benzene or toluene. Castor oil, sometimes added to increase the extensibility of the film, may be described as a softening agent. A cellulose lacquer like the older spirit lacquers, *e g* shellac in spirit, dries to a hard film by evaporation of the solvents, as distinguished from the oil varnishes which after the evaporation of the turpentine or other solvent dry by oxidation of the residual oil film.

Cellulose solutions, on the other hand, should consist of cellulose dissolved or dispersed in aqueous ammoniacal cupric oxide, zinc chloride, barium thiocyanate or in cold concentrated hydrochloric acid or other dispersing agent.

The cellulose lacquer industry has developed since the Great War, and, due to American enterprise, has attained considerable importance In 1933 there were manufactured in the United States, according to the latest census:

	U S gals.	Value, $
Clear cellulose lacquers	6,953,000	9,637,000
Cellulose lacquer enamels	7,423,000	15,518,000

In the same year the German output was valued at 21 8 million R.M The following particulars of production in the United Kingdom are obtained from the Fifth Census of Production (1935):

	1934		1935	
	gals	£	gals	£
Cellulose varnishes and lacquers.	1,911,000	880,000	2,014,000,	878,000
	cwt.	£	cwt	£
Cellulose enamels	123,000	821,000	130,000	851,00.

Industrial uses of collodium had been known since 1855 (A. Parkes, B P. 2359, 1855, and L. Cornides, B.P. 745, 1855), but although this and other nitrocellulose solutions had been in continued use, they were not important competitors of the spirit lacquers and oil varnishes. Only the large-scale production of low-viscosity nitrocellulose and of such solvents as *n*-butyl acetate and *n*-butyl phthalate made it possible to manufacture the types of cellulose lacquers described above. At this time, too, the American manufacture by mass production methods of motor cars, furniture and leather demanded quick drying finishes which could be applied by spraying.

The importance of the later stages in the history of the art may be shown by a brief review of the earlier solutions. Collodion was described by Schönbein (among others). He wrote to Berzelius on March 5, 1846, "One of the most peculiar transformations I have effected is in vegetable fibre which I have brought into such a condition that it is readily soluble in alcohol and ether, but unaffected by water, and if properly prepared possesses the transparency of glass" Surgical collodium as prepared in different countries contains from 2 to 4 g. of nitrocellulose dissolved in 100 c.c. of a mixture of alcohol and ether which varies from 1 : 8 to 1 . 3 by volume.

For experimental purposes where so rapid evaporation is not required, two volumes of ether to one of alcohol is common. Collodium has a number of minor surgical uses depending on its rapid production of a transparent waterproof film, and also on the facility with which it dissolves castor oil, Canada balsam or colophony (flexible collodium) or drugs such as salicylic acid. The "British Pharmacopœia" requires that the nitro-cellulose (pyroxylin) to be dissolved shall contain between 11 5 and 12 3% of nitrogen (a suitable percentage for lacquers) and that the viscosity at 20° of a 3% W/V solution in acetone shall be not less than 3 poises (*cf.* the viscosity of glycerol at 30°, 3 5 poises, olive oil at 15°, about 0 99 poises) Masson and McCall (J.C.S. 1920, 117, 823) measured the viscosity in poises (c g s. units) of a solution of nitro cellulose, N 12 2%: c=g/100 g acetone, η= viscosity

c	4·43,	5 05,	5 68,	6 31
η	35 5,	117 0,	305 0,	867 0

Acetone-, ethyl acetate, and acetic acid collodium each contain one solvent only. Acetone collodium exhibits the property of "blushing" or "chilling" (*i e.* drying to a film which is wholly or partly white and opaque. The rapid evaporation of the volatile solvent cools the residual solution below the dew-point of the atmosphere, water is deposited and dilutes the solvent so that the nitrocellulose is precipitated.

Ether-alcohol collodium was used until recently in the manufacture of artificial silk by the process of the late Count Hilaire de Chardonnet. It was also used in the preparation of the first photographic emulsion—the wet plate or collodion process of Scott Archer which survived the introduction of gelatine dry plates on account of its superiority for three-colour printing An important scientific use of collodium is in the preparation of membranes for ultra filters (molecular sieves) and dialysis, *e g.* of antitoxins, blood, etc. (Bechold, Z. physikal. Chem. 1907, 60, 257; Kolloid-Z 1931, 55, 172; M. Sigaud, Ann. Inst. Pasteur, 1929, 43, 190; Krueger and Ritter, J Gen Physiol. 1930, 13, 409; General Discussion of the Faraday Society, Trans Faraday Soc. 1937, 33, 1094, "Properties of membranes").

Ether-alcohol collodium exhibits a number of defects which have been overcome in the modern lacquers; it contains a very low percentage of solid residue, so that an extravagant quantity of highly inflammable solvent must not only be wasted but must pay freight to the consumer, it dries so quickly that it drags on a brush and cannot be spread evenly over a large surface. It deposits a film with a pronounced tendency to separate as a whole from a support, especially if this is bright metal or glass.

Amyl Acetate Lacquers.—Progress was made by J. H. Stevens in 1882, when on behalf of the Celluloid Manufacturing Company, U.S.A., he patented the use of a number of solvents, including amyl acetate (U.S.P. 269340) and a non-solvent, fusel oil (U.S.P. 269344). Technical amyl acetate, which contains the acetates of the alcohols found in fusel oil, is one of the best solvents for nitrocellulose; its boiling range, 100°–145°, indicates evaporation at a convenient rate (for vapour tensions of solvents, *see* Rechenburg, "Distillation in Theorie und Praxis." The chief objection to its use is the powerful odour of pear drops. Fusel oil, when purified to technical amyl alcohol, was from the first a valuable constituent of these lacquers, and prevented white drying. Added to modern lacquers it assists in dissolving shellac, sandarac, and other natural gums, also "ester gum" (*v.* p. 472) and glyceryl phthalate resin. Benzine, as a diluent, appears in Fields U.S.P. 381354, 13/8/1887, the proportions being propyl and butyl acetate 4 gals., benzine 4 gals., methyl alcohol 2 gals., pyroxylin 2½ lb.; acetone may be substituted for the methyl alcohol. In Imperial measure this formula is a 3% W/V solution of nitrocellulose. The same inventor adds shellac "on account of its adhesive properties" to a solution of nitrocellulose, 3% W/V, in amyl acetate, amyl alcohol, and methyl alcohol (U.S.P. 422195, 25/2/1890). Lacquers of the last mentioned types and known as "cold lacquers" were in use in Birmingham about 1900; to some extent they replaced spirit-shellac lacquers ("hot lacquers"), which were dried in hot air. Nitrocellulose at this time was the high-viscosity variety, and could be purchased damped with 30% methylated spirit, so that the dangerous operation of drying was avoided when the formula contained alcohol. That low-viscosity nitrocellulose of satisfactory quality in all respects would open up a wide field for nitrocellulose lacquers was known both in England and the United States, the available collodium cotton yielding solutions which were too viscous for use as lacquers at concentrations beyond about 6 to 8 oz. per imperial gallon. A low-viscosity nitrocellulose had, however, been made by a method that was both uneconomical and dangerous—nitration with a hot acid bath (Tucker, Ind. Eng. Chem. 1921, **13**, 624). This author describes the use in the leather industry of a 40-second nitrocellulose defined by the viscosity of a solution of 1 lb. nitrocellulose in one U.S. gallon of mixed solvent 70% ethyl acetate and 30% benzene, determined by observing the time of fall of a steel ball $\frac{5}{16}$ in. diameter through 10 in. of the solution (*cf. infra*). The solvents for the coating solution were acetone oils, benzene and alcohol. By 1925 the half-second nitrocellulose had appeared in America (Keyes, Ind. Eng. Chem. 1925, **17**, 558; for patents *v.* Applied Chemistry Reports, 1926, **11**, 132). The solid content of lacquers could now be increased to 32 oz. per U.S. gallon (38·4 oz. per imperial gallon) consisting frequently of about 22 oz. half-second nitrocellulose and 10 oz. of resin, so that the required weight of dry finish on a wood surface could be obtained in three coats. The four common types of nitrocellulose available were (1) alcohol-soluble with 11·5 to 11·7% N and a viscosity of a half-second; (2) R.S. (regular soluble) nitrocellulose of the same viscosity but with 12·0 to 12·2% N; (3) Dope nitrocellulose with 11·8 to 12·4% N and a viscosity of 15 to 30 seconds; (4) lacquer nitrocellulose containing 11·8 to 12·4% N with a viscosity of 60 to 80 seconds.

Uses.—(1) For lacquers containing resins which require a low ester and high alcohol content in the active solvent; (2) for modern wood and metal lacquers; it is soluble in esters and ketones alone or when mixed with alcohol; (3) chiefly for coating artificial leather; (4) in the older type of brass and metal lacquers, for many years.

The resin constituents (gums for spirit and oil varnishes) are added to give the film a brilliant gloss hardness, adhesion, and body, and to render it more impervious to water. The hardness of the film may be increased so that it can be rubbed down as with the coach type of oil varnishes. With increasing resin content the film tends to be brittle, but addition of resins does not raise the viscosity to the unmanageable values of the older nitrocellulose lacquers—the effect on viscosity of 8 oz. of nitrocellulose has been compared to that of 32 oz. of shellac—figures which would be influenced greatly by the nitrocellulose, solvents, and diluents employed. Good adhesion, not a property of nitrocellulose solutions, is obtained by adding gums such as shellac, elemi, kauri, etc., less efficient are sandarac and mastic. Dammar is described as yielding a soft and tough film, while additions of rosin, as with oil varnishes, may produce brittleness.

Keye's (*l.c.*) classification of solvents into the following classes is based on the boiling-points quoted, although vapour tensions at room temperature would correspond better to practice. *Low Boilers* (b.p. $<$100°).—Ethyl acetate, 77°; ethyl alcohol, 78°; acetone, 57°; benzene, 80°. *Medium Boilers* (near 125°).—Diethyl carbonate, 125°; butyl acetate, 125°; amyl acetate, 138°–142°; butyl alcohol, 117°; amyl alcohol, 126°–132°; toluene, 111°. *High Boilers* (b.p. between 150°–200°).—Ethyl lactate, 155°; diacetone alcohol, 164°; xylene, 143°. *Plasticisers* and *Softeners* (boiling near 300° or above).—Tricresyl phosphate$>$350°; triphenyl phosphate $>$325°; diethyl phthalate, 290°; dibutyl phthalate, 340°; diamyl phthalate$>$340°; triacetin, 267°. The three non-solvents of nitrocellulose, benzene, toluene, xylene, are included because of their solvent action on resins, and possibly because of their effect in admixture with ethyl alcohol (in which mixture nitrocellulose partly dissolves).

The value of the low boilers is in reducing the viscosity of spraying lacquers, and in evaporating quickly; being the least expensive ingredients, they serve to reduce costs. Flowing of the lacquer to form a uniform smooth surface is partly due to the medium boilers, while the high boilers not only assist flow but are residual solvents which retain the nitrocellulose and resin in solution, and thus prevent blushing or white drying due to precipitation of both or

either ingredient. The deposit of water from the atmosphere, due to the cooling effect of the evaporating solvents, may be re-evaporated as an azeotropic mixture of, for example, benzene, alcohol, and water, before precipitation can occur. The non solvents of nitrocellulose, butyl and amyl alcohol included in the medium boilers are useful for preventing blushing and as resin solvents. There is scope for much ingenuity in so formulating the lacquer that the effects of changes in composition during evaporation are compensated, while at the same time the cost is reduced by the presence of as much inexpensive diluents as the final effect permits.

Dilution Ratio or Solvent Power is a measure of the maximum volume of a diluent which can be added gradually without causing precipitation to a well stirred nitrocellulose solution at a specified temperature (20°). The volume of diluent divided by the volume of solvent (*e g* 20 c c in which 2 g half second nitrocellulose had been dissolved) gives the required figure. The value of a diluent to the lacquer manufacturer is proportional to the dilution ratio in which it plays a part. Davidson and Reid (Ind Eng Chem. 1927, 19, 977) confirmed the opinion that greater volumes of diluent aromatic hydrocarbons than of petroleum hydrocarbons can be added. They found, for example, that the monoethylether of ethylene glycol has a dilution ratio of 5 2 for toluene and 0 8 for gasoline Keyes (*l.c.*) measured the number of c c of toluene added until a turbidity persisted in 100 c.c. of solutions of the following solvents of R S nitrocellulose (*v supra*) 240 g per litre (32 oz per U.S. gallon) and reported diethyl carbonate, 150, butyl acetate (85%), 240, amyl acetate (85%), 280; diacetone alcohol, 340, tricresyl phosphate, 380, diethyl phthalate, 480, ethyl lactate, 700 Brown and Bogin's (*ibid* 1927, 19, 968) determinations were carried out to give the dilution ratio at a final concentration of about 8% nitrocellulose (ordinary lacquers have 8 to 12%). Under these conditions the ratio for added toluene is 2 93 for *n* butyl acetate as solvent, 3 80 for ethyl lactate, 8 00 for dibutyl tartrate. When employed as a diluent, butanol (*n*-butyl alcohol) gave a dilution ratio with *n* butyl acetate, 8 2, ethyl lactate, 10 2, dibutyl tartrate, 15 0

Viscosity.—The nitrocellulose is usually purchased damped with 30% of ethyl or of isopropyl alcohol, it is dried before making up the standard solution The usual classification from ½ second upwards is based on the falling sphere method applied to a standard solution and is due to the Hercules Powder Co, U S A This solution contains nitrocellulose, 12 2%, alcohol, (95%), 22 0%; ethyl acetate (99%), 17 5%; benzol (90°), 48 3%, all W/W% It is placed in a glass tube 14 in long and 1 in in diameter, having marks 2 in from each end, contained in a bath of 25°. A steel ball (ball bearing) $\frac{5}{16}$-in diameter, weighing, about 2 05 g, is dropped axially into the solution and falls between the two marks, 10 in. apart, in a time which is measured in seconds by a stop watch

In Nobel's method 3, 10, 20, 40, or 60 g of nitrocellulose in order of decreasing viscosity of the samples are dissolved in 100 ml. of aqueous acetone, d_4^{20} 0 8097 (nearly 95% v/v). The steel ball is $\frac{1}{16}$-in. diameter and the time of fall (t) through 15 cm. of the solution at 20° is observed, the tube used resembles that described in B S.S 188, 1937, "Determination of Viscosity," p 24. The time is calculated to viscosity in c g s units based on (t) 19 seconds, for castor oil, d^{20} 0 96; with the dimensions chosen, $t/2$ for the nitrocellulose solution is for practical purposes equal to the kinematic viscosity in stokes

The half-second nitrocellulose of the Hercules Powder Co corresponds to an I C.I. product with 11 8 to 12 3% N, of which 40 g dissolved in 100 ml. of 95% acetone yield a solution with a kinematic viscosity of 45 c g s units The relation of apparent viscosity to ease of application is shown by Mardle's figures (J Oil Col Chem. Assoc 1935, 18, 12) A viscosity of 4 to 5 poises at 20° appears to be suitable for brushing to yield a film weight on metal of 1 oz. per sq yd and a viscosity of about 3 poises for spray application using 50 lb per sq in air pressure (To convert the units dynamic viscosity in poises—density=kinematic viscosity in stokes)

For recent work on the viscosity of solutions of nitrocellulose *see* papers by Staudinger and other authors in "Colloid Aspects of Textile Materials," General Discussion, Trans Faraday Soc 1933, 29, 18, 32, 110, 122, Staudinger and Sorkin, Ber 1937, 70, [B], 1993, Philipoff, Angew Chem 1936, 49, 855, Taniguchi and Sakurada, J Soc Chem Ind. Japan, 1937, 40, 121B, Shinoda and Inagaki, Cellulose Ind 1936, 12, 256, Houwink and Klaassens, Kolloid Z 1937, 79, No 2, 138 The patented processes for reducing the viscosity of nitrocellulose are reviewed by Major, Rev gen. mat plast 1936, 12, No 7, 199

M. G. Milliken (Ind Eng Chem 1930, 22, 327) describes the manufacture of nitrocellulose of low viscosity by the Hercules Powder Co, Wilmington, Del, U.S.A Experimental heating of mixtures of nitrocellulose in water, in autoclaves revealed the connection between time of heating, temperature, viscosity reduction, and degree of denitration (Fig 1) The decomposition products are removed by subsequent washing, in contrast to methods of reducing the viscosity of nitrocellulose in solution At one time brick lined steel digesters were in use holding 4,000 lb of nitrocellulose and 60,000 lb of water, but difficulties were experienced in providing adequate removal of the gases arising from the denitration which accumulated in the fibrous nitrocellulose causing false water levels and dry spots in the digesters To avoid these hazards, a continuous process was adopted in which the suspension of nitrocellulose and water is pumped through a 4-in pipe 4,000 ft long, heated by a steam jacket for a distance at the entrance end and cooled by a water jacket near the exit end. A stand pipe 200 ft high is connected to the exit, and at the top the mixture of water and nitrocellulose overflows into a descending pipe delivering into tubs below (Fig 2) Reduction to half second viscosity is obtained in 25 minutes, which is the time of travel through the pipe. A section of Pyrex

tubing in the coil near the exit enables the velocity of the material to be observed (Fig. 3). The coils of the continuous digester (Fig. 4) designed to prevent the formation of gas pockets,

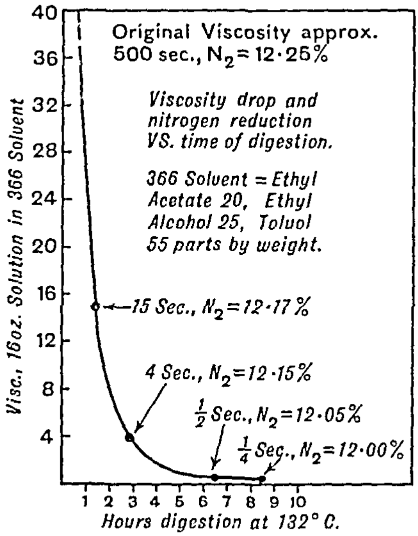

FIG. 1.

contain a charge of 600 lb. nitrocellulose (*cf.* B.P. 301267, 338941, Hercules Powder Co., Assees of M. G. Milliken).

The types of nitrocellulose were again

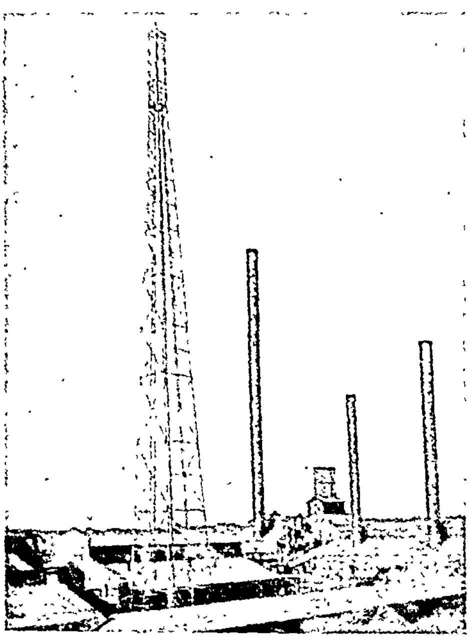

FIG. 2.—TOWER SUPPORTING BACK-PRESSURE. STAND PIPE

classified by Partridge (Ind. Eng. Chem. 1929, 21, 1044); half-second and four-second for motor car and wood-finishing lacquers, eight-second for wood lacquers, fifteen-second for increasing the body of a lacquer or for imparting waterproofing properties to shellac solutions. Forty-second and seventy-second types were specially prepared to avoid the usual gelatinisation when mixed with bronze powders, twenty-second and seventy-second for dipping lacquers for silver, dope nitrocellulose in the wide range of viscosities 20 to 200 seconds.

Solvents.—The name of one of the low boilers might be misunderstood—it is "methyl acetone,"

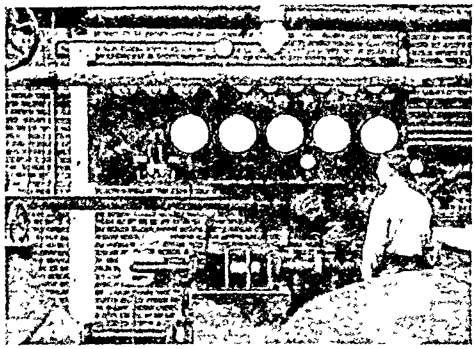

FIG. 3.—TEMPERATURE AND PRESSURE CONTROL BOARD

In case the Pyrex tube, with nitrocellulose-water mixture passing through

this is a mixture of varying proportions of acetone, methyl alcohol, and methyl acetate. The former *B.E.S.A. specification 2D1 stated* the following properties: d^{15} 0·830; b.p. 50°–70°; acetone 45–60%; clearly soluble in water in all proportions.

As a result of the success of the Commercial Solvents Corporation in working the Weizmann process (for history, *v.* Gabriel and Crawford, Ind. Eng. Chem. 1930, 22, 1163) of fermenting

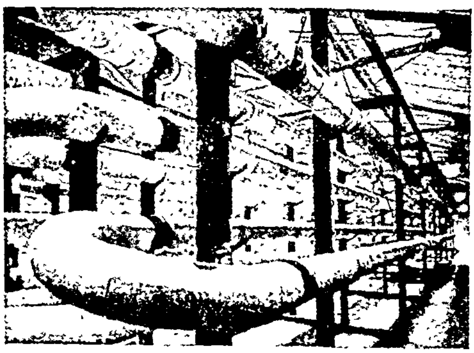

FIG. 4.—CONTINUOUS DIGESTER COILS

maize starch to give acetone and *n*-butyl alcohol, this alcohol and hence the corresponding acetate and phthalate became available in large quantities for the lacquer industry (for manufacture from acetylene, *v.* Vol. I, ACETYLENE, ACETALDEHYDE). The supplies of "amyl" alcohol and "amyl" acetate were increased by a synthetic process starting from a mixture of *n*-pentane and *iso*pentane.

*cyclo*Hexyl acetate and methyl*cyclo*hexyl acetate resemble amyl acetate. Methyl ethyl ketone was well known as a solvent before and during the Great War, compared with acetone its slower evaporation renders it less liable to blushing, but its dilution ratio with benzene is lower, being 4·6 9. *cyclo*Hexanone and methyl*cyclo*hexanone have dilution ratios with benzene even higher than acetone, 8 6 and 8 0 respectively according to the measurements of Nobel's Explosive Co

Bogin (Paint, Oil and Chem Rev. 1936, 98, No. 10, 9) states that the usual diluent is now a mixture of equal parts of toluol and naphtha Since butyl acetate tolerates additions of this mixture better than ethyl acetate, the latter solvent has lost any advantage it formerly possessed as an ingredient for reducing viscosity

The properties of a lacquer film depend partly on the retention of solvents, which itself is influenced by the nature and amount of the plasticisers Bogin and Wampner (Ind Eng Chem, Ind Ed. 1937, 29, 1012) found the solvents retained at no flow point amounted to 20–35% of the weight of the film, at dry point 12–20%, and after three weeks' ageing 5–8%

The properties of solvents and diluents and the prevention of blushing are considered by B K Brown (Ind. Eng Chem 1928, 20, 183) and by Davidson and Reid (*ibid* 20, 199) Two instances of formulæ will be given The solvent mixture used by Rogers and Banta (*ibid* 20, 198), contained ethyl acetate 10 parts, butyl acetate 25, dibutyl phthalate 5, butanol 10, toluene 31. The solids were half second nitrocellulose wet with 30% alcohol 8 parts, ester gum 7, cumar resin 4

B. K. Brown (*ibid* 1925, 17, 568) prepared a mixture of butyl acetate 25%, ethyl acetate 15%, butanol 10%, toluene 42%, xylene 8% The finished clear lacquer contained the following solids dissolved in one (U S) gallon of the mixed liquids nitrocellulose (28 seconds) 8 oz, dammar, 9 oz; "ester gum," 2 oz

British Standard Specifications —The following have been issued for solvents and diluents, those listed with D numbers relate to aircraft dope and ingredients, *i e* primarily to cellulose acetate solutions clear or pigmented.

Low Boilers —Acetone, 3D22 and 509, 1933, ethyl acetate, 533, 1934, methyl ethyl ketone, 3D1; "methyl acetone," 2D1; ethyl alcohol 3D9 and 507, 1933, methyl alcohol, 506, 1933, benzol 3D10

Medium Boilers —Normal butyl alcohol (butanol), 508, 1933, butyl alcohol, 2D17, butyl acetate, 3D4; normal butyl acetate, 551, 1934; amyl acetate, 3D3 and 552, 1934.

High Boilers —Diacetone alcohol, 549, 1934, ethyl lactate, 663, 1936

The chief absentees are amyl alcohol (B S S 696 for this substance relates to milk analysis), *iso*propyl alcohol, ethylene glycol monoethyl ether and its mono acetate, *cyclo*hexanone and methyl*cyclo*hexanone, toluene, xylene, and ligroin

Plasticisers (plastifiers) for purposes of classification are substances which gelatinise nitrocellulose and are retained to a greater or less extent by the lacquer film after the evaporation of the solvents The typical plasticiser is camphor, which plays an essential part in the manufacture of celluloid, and is therefore contained in lacquers made by dissolving celluloid scrap or film scrap containing camphor. It is impossible to draw a sharp distinction between plasticisers and high boiling solvents.

British Standard Specifications have been issued for the following substances: diethyl phthalate, 574, 1934; dibutyl phthalate, 573, 1934, triacetin, 2D11; triphenyl phosphate, 3D12. Castor oil (for nitro dope coverings) is specified in 3D5 but is a softening agent rather than a plasticiser as it exudes from the film if present in high percentage of the nitrocellulose Blown castor oil, largely used in leather cloth lacquers, and the important tricresyl phosphate are not the subjects of British Standard Specifications Triphenyl phosphate is specified in 3D12.

A Kraus (Farbe u Lack, 1937, No. 5, 9; No 7, 79, No. 8, 89) while confirming the satisfactory properties of dibutyl phthalate considered diphenyl phthalate to be the best of the plasticisers tested in cellulose enamels. Triamyl citrate also gave good results in enamels containing dammar Benzyl butyl phthalate and triphenyl urea improved the resistance of the films to weathering References are given to patent literature In an earlier publication (*ibid* 1934, 39, 53) this author compared 41 plasticisers of nitro cellulose including butyl tartrate and butyl oleate, these gave satisfactory elongation and tensile strength of the film. Previously (*idem*, *ibid* 1933, 545, 556) it was found that the yellowing of nitrocellulose films and the extent of decomposition on exposure to ultra violet light was not parallel with the alteration in mechanical properties Volatility of the plasticisers and the durability of the films were not directly proportional to one another (*ibid* 1934, 279, 291) Pfeiffer and Speicher (Paint, Oil and Chem Rev. 1936, 98, No 10, 16) state that although nitrocelluloses of ¼- and ½-second viscosity yield relatively weaker films, their use in lacquers permits the solid content of a spraying lacquer to be considerably increased Ratios of resin to nitrocellulose of 3 2 (Farben-Ztg 1936, 41, 56) and 2 1 (Nitrocellulose, 1936, 7, No. 1, 35) have been specified in Germany

Resins (Varnish Gums) —Strong solutions of the resins in the diluents are convenient for mixing with the solution of nitrocellulose in solvents and plasticisers, and permit the removal of wax from shellac and dammar Other natural resins used are elemi for flexibility, and mastic The most important synthetic resin, "ester gum" (prepared by heating glycerol, and rosin), is very soluble in benzene. Shellac may sometimes be substituted by a phenol-formaldehyde resin Glyptals, prepared by condensing phthalic anhydride and glycerin, are much used in the form of alkyd resins of the type made by condensing glycerol with phthalic anhydride and fatty acid from a non-drying oil. Their effect is to increase the gloss, adhesion and fastness to light of cellulose lacquers, in which they can substitute part of the nitro-

cellulose and plasticiser (Bond, J. Oil. Col. Chem. Assoc. 1936, **19**, 225).

Glyptals containing unsaturated acid groupings from drying oils are used in priming lacquers on wood. Cellulose undercoats were unsuccessful in Mardle's tests, (*ibid.*, 1935, **18**, 12) and adhesion on metal surfaces was best obtained when ordinary linseed oil paints formed the undercoating.

Cellulose Enamels (Pigmented Cellulose Lacquers) are manufactured with the aid of the ordinary grinding plant of a paint factory by grinding together the pigment and liquid plasticiser and mixing the paste with the nitrocellulose solution containing the remaining ingredients.

B. K. Brown (*l.c.*) prepared an enamel by first grinding 3–4 lb. zinc oxide in a ball mill with the nitrocellulose solution already described (*v. supra*) and then adding the diluents. (In this method of grinding evolution of nitrous fumes sometimes occurs.) The resulting enamel gave a film which cracked on bending, but on adding 6·5 oz. dibutyl phthalate a highly flexible coating was obtained. W. Toeldte (Farben-Ztg. 1931, **37**, 448) records the results of numerous tests of cellulose enamels.

Cellulose Acetate, containing acetyl groups equivalent to about 54% $C_2H_4O_2$, dissolved in a mixture of acetone alcohol and benzene with a small proportion of benzyl alcohol and triphenyl phosphate, has been largely used for doping the wings of aircraft. The coated linen becomes taut and rigid as the solvents evaporate. The cellulose acetate layers were then covered with a coating of a pigmented nitrocellulose solution containing amyl acetate and castor oil. The khaki pigments (ochres and red oxide of iron) absorbed the ultra-violet rays of sunlight and were used because F. W. Aston showed that the unprotected cellulose acetate layers were transparent to ultra-violet, rays which caused the deterioration of the linen fabric.

Relevant British Standard Specifications are: cellulose acetate, 2D50; properties of aeroplane doping scheme, 2D101; nitrocellulose syrup, 2D8; yellow ochre, D26; zinc oxide, 2D27; red oxide of iron, 2D28; identification red, 2D29; carbon black, 2D30; ultramarine blue, 2D31; aluminium powder, 2D32. An Air Ministry specification for cellulose finishes is D.T.D.63.

Cellulose Ethers.—The great stability of ethylcellulose and of benzylcellulose and the solubility of certain types in the cheaper solvents benzene and alcohol are desirable properties, but no commercial lacquers containing these ethers are recorded by Traill (J. Oil Col. Chem. Assoc. 1936, **19**, 248).

Application.—Dipping.—Electroplated silver articles as well as brass and bronze goods are often finished by dipping in a dilute colourless quick-drying lacquer, removed, allowed to drain, and dried in an oven at about 60°. An invisible protective film remains on the goods which prevents tarnishing during storage. Defects of the process are "greening" if the lacquer is acid, or an iridescence due to "Newton's Rings" if the lacquer film is too thin. Coloured transparent lacquers are unsuitable for dipping, for differing shades of colour are seen where the film is of uneven thickness. Colour can be imparted by immersing the dipped goods in solutions of basic dyes for a few seconds and then washing in water. Pencils, penholders, walking sticks, metal and wood knobs, toys are dipped mechanically by means of a device holding a number of the articles. Wings of motor cars are also dipped as part of a continuous process of manufacture.

Brushing.—This method is used for coating optical instruments, embossed name plates, metal parts of aircraft, toys, lampshades, with clear or pigmented lacquer, in some cases above an undercoat of an oil paint type, and for doping airplane wings above a coating of diluted dope (cellulose acetate solution).

Spraying.—For the mass-production of motor cars, furniture, coated leather, and many small articles, quick drying finishes, rapidly applied by spraying, are essential. Spraying may be hand-operated or mechanical, and must be carried out in a suitable, rapidly renewed atmosphere, *e.g.* in spraying cabinets adequately ventilated so that no mixture of vapour and air can form, which would be noxious to breathe or capable of exploding by an electric spark or a flame ("Explosive Properties of Lacquer Solvent Vapour," Richardson and Sutton, Ind. Eng. Chem. 1928, **20**, 187; *v. infra*, Regulations). The spray gun or pistol comprises a nozzle connected with a cup or container for the lacquer and also with a flexible pipe supplying compressed air, the cup and nozzle being mounted on a hollow handle which is the air inlet. The lacquer is projected in a fine spray (like that from an atomiser), fan-shaped for covering large surfaces or as a narrow jet. Compared with brushing, a thinner coat and better adhesion are obtained with lower cost for time and material.

Regulations regarding fire hazards, etc., and dangers to health.—Explosives Act, 1875, Section 3, Note A.—Collodion cotton in solution in ether and alcohol or wet with water, or saturated with methylated spirit is not within the meaning of the Act; "Memorandum on the Manufacture, Use and Storage of Cellulose Solutions," Factory Department of the Home Office; "General Railway Classification of Goods"; "Classification of Dangerous Goods by Merchandise Trains"; "Carriage of Dangerous Goods in Ships," Board of Trade Notice 130, 1933; Regulations under the Petroleum Acts, Home Office, 1934, define an inflammable liquid for use in cellulose solutions to mean any liquid which in the official test (Second Schedule to the Petroleum (Consolidation) Act, 1928, [a]) gives off an inflammable vapour below 90°F.; A Guide to the Factories Act, 1937, H.M. Stationery Office.

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CELLULOSE PLASTICS.

CELLULOSE ESTER PLASTICS

INTRODUCTION—The cellulose esters which have developed to industrial importance are nitrocellulose and cellulose acetate The industrial exploitation of both esters has developed very rapidly during the present century At the beginning of this century the major industrial application of nitrocellulose, apart from use in explosives, was in the manufacture of celluloid Cellulose acetate has been known since 1865 During the War it was used in the manufacture of aeroplane dopes, but since then it has become of commercial importance

The outstanding feature in the manufacture of nitrocellulose celluloid is the use of camphor, which is a unique plasticiser. Cellulose acetate celluloid has two advantages over ordinary *nitrocellulose celluloid—non-inflammability* and freedom from discoloration on exposure to sunlight, but has the disadvantage of lower tensile strength. The inflammability of celluloid has proved a serious drawback. Many large stores now refuse to stock celluloid articles because of the fire risk Consequently synthetic resins have been used in the manufacture of many articles previously made in celluloid.

The discoloration of nitrocellulose celluloid *is a drawback in some uses of clear celluloid,* for instance, in safety glass interlayers. Certain types of green glass, which lessen the passage of actinic rays, have been employed in order to reduce the rate of discoloration of the celluloid interlayer. Other manufacturers, however, have preferred to use a cellulose acetate interlayer. More recently the laminated type of safety glass has been largely replaced in Britain by heat hardened glass

Photographic and cinema films are still made principally from nitrocellulose. Certain "safety" films are made from cellulose acetate, and cinema films for home use must be made from this ester. Scrap cinema film is employed by some manufacturers for the preparation of lacquers, enamels and leathercloth, but most manufacturers prefer to start from a nitrocellulose of known properties Cellulose acetate is also cast into thin films, 0 001 in thick, used for wrapping and for electrical purposes

Another type of cellulose acetate film now prepared is one which has a strengthening layer of wire netting These films are used in cold frames and greenhouses, being lighter and cheaper than glass and, in addition, being claimed to have the advantage that the cellulose acetate permits the passage of more ultra violet light

Sheets of celluloid are moulded into various articles—toothbrush handles, brush backs, *trinket boxes, etc, at a temperature* of about 220°F. Attempts made to prepare nitrocellulose moulding powders have not been very successful Fire retarding plasticisers, such as tricresyl phosphate, and fillers such as gypsum have been used to reduce the inflammability. The moulding conditions are difficult and temperatures above 120°C are dangerous Cellulose acetate, on the other hand, is the basis of various types of thermoplastic moulding powders which are widely used especially in injection moulding.

The first artificial silk (or rayon) of any importance *was made from nitrocellulose by the* Chardonnet process. The nitrocellulose was dissolved in an alcohol ether mixture and spun into filaments by extruding through glass capillaries After twisting, the yarn was denitrated in a mixture of sodium and ammonium hydrosulphides This Chardonnet process was gradually displaced by the cuprammonium and later by the viscose process and was finally abandoned in 1933 A very important part of the rayon output is now made from cellulose acetate. In all these industrial applications the cellulose acetate is the partially hydrolysed acetone soluble type *with an acetyl value of* 52–56%, calculated as acetic acid

The production of low viscosity nitrocelluloses, viscosity 10–140 c g s measured in 40% solution in 95% acetone, speeded the use of nitrocellulose in the lacquer industry. Spraying, brushing and dipping lacquers and enamels have been

prepared, but the greatest production is in the spray type for car finishes, furniture finishes, and interior decoration. Synthetic resins, particularly the phthalic anhydride-glycerol type, have gradually made inroads into this field, and some makes of cars are now being finished in synthetic resin compositions. Nitrocellulose dopes are also used in the shoe industry as adhesives, as stiffening dopes for toe-caps, etc., and as lacquers for grain and split leathers.

Cellulose acetate has a restricted use for special types of lacquers. The two principal disadvantages of cellulose acetate in lacquer manufacture are the brittleness of films made from low viscosity cellulose acetate and its incompatability with resins.

Recently a type of celluloid flake has been used in enamel manufacture. The advantages of such "nitrocellulose chips are that the pigment has been thoroughly dispersed and thus grinding operations are eliminated.

Various fabrics are coated with cellulose esters to produce bookcloths, artificial leather, etc. Nitrocellulose is principally used, the softener being castor oil, which gives the required softness without stickiness in the final product. Papers are also coated with nitrocellulose composition to attain water-proofness, moisture-proofness, decorative effects, etc. The widest outlet of this kind is at present in the coating of viscose film to render it moisture-proof.

The foregoing industrial applications of cellulose esters have all been processes where solutions have been employed. This means that special precautions have to be taken to deal with the fire hazard from inflammable solvents. It also means that there is an expensive loss of solvent unless a solvent recovery plant is used, and the latter is only justified in large factories. To overcome these disadvantages to some extent and to obtain certain working advantages, such as the use of higher viscosity lacquer base, aqueous emulsions of nitrocellulose lacquers have been prepared. This new method reduces the cost of manufacture of the coating composition, enables the application of a greater weight of solids for a given solvent cost, and reduces the fire risks in manufacture.

The properties of cellulose esters and cellulose ethers are compared in the section Cellulose Ether Plastics.

Nitrocellulose Chips.

Celluloid-like granules or flakes, clear and pigmented, are now marketed for lacquer and enamel manufacture and are generally known as nitrocellulose chips or flakes. The clear chips are celluloid-like flakes consisting of nitrocellulose and plasticiser. To prepare a lacquer the chips are dissolved in organic solvents, and resins, etc., are added to complete the formulation.

The pigmented chips, however, are claimed to have such advantages as improved dispersion of pigment, freedom from settling in the final lacquer, better colour, and better weathering properties. The dispersion and wetting of pigments in vehicles is the most important part of paint manufacture, and to effect this dispersion paint factories are equipped with various grinding machines, rolls, ball mills, etc. The difficulty of this grinding and wetting out process becomes more evident when one considers that 1 g. of spherical pigment particles 0·7 micron in diameter and of density 4·2, titanium dioxide for example, presents a surface area of 2·44 sq. yds. and in the case of some carbon blacks 1 g. of pigment may have a surface area of about 160 sq. yds. Black chips are the best known type although various colours can be obtained. Carbon black manufacturers have developed chemical and mechanical methods of colloidally dispersing the pigment in lacquer vehicles of nitrocellulose and plasticiser, the product being in the form of dry, brittle, black flakes.

The nitrocotton employed varies in viscosity according to the ultimate application of the enamel, but is generally of the low viscosity type, viscosity around 40 c.g.s. measured in a solution of 40 g. in 100 c.c. 95% acetone. Various common plasticisers such as dibutyl phthalate are used. The pigment content varies and the approximate composition range is:

	%
Nitrocellulose	55–67
Plasticiser	20
Carbon black	25–13

In the preparation of enamels from these chips the operation of grinding is eliminated. The chips are preferably dissolved and dispersed in a viscous medium. This may be done by dissolving them in a solution of nitrocellulose in a rich solvent mixture; or alternatively by soaking the chips in a relatively small quantity of solvent mixture containing a very small proportion of true solvent for nitrocellulose, thus causing the chips to soften and break up. The remainder of the solvent and the other enamel constituents are added to the viscous syrup. These operations are carried out in tanks fitted with slow stirring apparatus, continuously in motion. The enamels can be made by simply adding the chips to the entire mixture of solvent, etc., but in such a case the preparation will take longer, since there will be a tendency for the chips to become tacky in the rich solvent, stick together, and form lumps which dissolve only slowly.

The advantages which are claimed for enamels made from these chips are:

(1) Greater depth of colour.
(2) Greater resistance to exposure.
(3) Greater gloss, rendering polishing unnecessary.

Linoplastic.

A nitrocellulose composition is the basis of certain types of linoleum. The nitrocellulose plastic replaces, partly or wholly, the linoxyn which is the binding material in ordinary linoleum. The type of linoleum thus produced has better wearing properties, greater flexibility, and greater resistance to washing. The nitrocellulose used has a nitrogen content of about 12·2% and a viscosity of about 40 c.g.s. in a solution of 20 g. in 100 c.c. 95% acetone. The nitrocellulose is mixed with plasticisers and softeners such as tricresyl phosphate and castor

oil, the former being chosen for its fire retarding properties. A typical mixture contains 35% nitrocellulose, 15% tricresyl phosphate, and 50% castor oil. The plastic thus formed is incorporated on rolls with cork dust and yellow ochre, the proportion being approximately 33 : 50 : 17. Further quantities of filler, etc., may be added as desired (B.P. 349984).

Cellulose Acetate Moulding Powders.

Composition and Method of Manufacture.—The cellulose acetate employed in the manufacture of moulding powders is the normal "rayon" type, having an acetyl content corresponding to 52–56% acetic acid, a hygroscopicity of about 11–12%, and a m p of 220°C, above which temperature it chars Scrap cellulose acetate rayon, celluloid, and films have been employed, but generally in the cheaper types of moulding powders and in black and the darker colours, where the colour of the starting material does not matter For use in most moulding powders the cellulose acetate is received in a granular condition, its softening point is lowered and its flexibility increased by incorporating plasticisers such as tricresyl phosphate, triphenyl phosphate, dibutyl phthalate, diethyl phthalate, or triacetin. The quantity used is about 50% of the weight of acetate but varies according to the quantity of filler present.

Incorporation is generally carried out in a mixer of the Werner Pfleiderer type, and a quantity of solvent, acetone, is added to help the mixing Fillers, generally inorganic materials such as zinc oxide, china clay, barytes or blanc fixe are added. The quantity varies, being about 0.5% in translucent materials, and 2–3% in normal opaque materials, but is greater in the cheaper class of moulding powder. Fillers, in general, while contributing to the desired colour, translucency, or opacity, increase the density of the composition, reduce the tensile strength, and increase the brittleness of the moulding. Colouring materials are added and include inorganic pigments, lakes and dyes. The colouring materials must not deteriorate at the temperatures of incorporation and moulding, *e.g.* must withstand temperatures up to 150°–160°C. A small amount of wax 0.1–0.5% may be added to ease the removal of the moulding from the mould and to increase the polish.

The plastic formed by preliminary mixing, which may take 10–30 minutes, is given a second incorporation on steam-heated rolls, of the type used in rubber mixing. Very thorough mixing takes place during this process The cellulose acetate is thoroughly plasticised, the pigment dispersed, and the bulk of the solvent removed. The rolls are cored and provided with steam heating and water cooling. There is a certain amount of frictional heat. The rolls are heated to a temperature of 140°–150°C, the plastic being at a temperature of 120°–130°C. The rolls run at differential speeds, the front roll speed generally being 20–25 r.p m, the back roll 15–20 r.p m, the speed varying with the size of the rolls. The front roll is kept the hotter and the crêpe of plastic sticks to it. Colouring materials may sometimes be added at the rolling stage in order to produce special effects. The plastic is rolled into a thin sheet which is removed from the rolls, generally provided with scraper blades for the purpose. This crêpe from the rolls is allowed to cool and then broken into pieces 3–6 sq in. in area, either by hand or by passing through a machine of the coke-crusher type. In certain cases, for example, production of tortoiseshell effects, the differently coloured plastics are used in such sizes in compression moulds. For most purposes, however, these larger pieces are ground, in a hammer type of disintegrator, to pass through a 20 mesh sieve.

Moulding.—Cellulose acetate plastics are permanently fusible. In moulding them the composition, generally in the form of a granular powder, is heated to approximately 130°–160°C. and pressed into the shape of the mould. The moulding is then cooled under pressure and sets more or less hard before removal There are two distinct methods of moulding such cellulose plastics, compression moulding and injection moulding, and each has its own particular use Compression moulding is employed principally in the case of large or medium sized mouldings of relatively simple shape. Injection moulding is used for the production of small articles or for articles of intricate shape

Compression Moulding.—Compression moulding, alternatively known as "hot and cold pressing," is a relatively simple process The moulding powder is poured into a heated mould, the mould closed, heat maintained until the powder has become plastic and has filled the mould, which is generally fitted with a channel into which the excess or "Flash" flows. Pressure is applied and maintained while the mould and contents are cooled. The mould is generally cored and steam and cold water can thus be run through alternately during the moulding cycle One of the best examples of this type of moulding is in the gramophone industry, where shellac compositions are moulded into gramophone records at a rate of 60–80 per hour. The pressure exerted during the moulding of cellulose acetate powders is approximately ½ ton per sq. in The polish of the article depends on the polish of the mould. The mould is generally chromium plated and the moulding needs no after polishing, save at edges.

Injection Moulding.—In this method of moulding the powder is run into a chamber, heated by a coil at 160°C., where it becomes plastic. It is then forced at great velocity through a narrow orifice into a cold mould. The mould is made of heavy masses of metal which require no cooling. The plastic is forced into it under considerable pressure, 7–10 tons per sq in. Not only is it possible to mould small and intricate shapes quickly in this way, but the finished moulding has increased tensile strength and elasticity compared with a similar composition moulded by the compression method. A description of moulding machines and moulds is given in "British Plastics Year Book," 1932, p. 57. These machines can be made to work automatically and the moulding time reduced to 15 seconds. The mould output per impression may be as much as 8 times that of standard compression moulds with thermo-

setting materials. Certain mouldings, such as those for electrical work, have metal inserts.

Properties.—The following table of properties, which is abstracted from Chem. Met. Eng. 1932, 39, 656, refers to "cellulose acetate press (*i.e.* moulding) powder."

Compression ratio— $\frac{\text{volume loose powder}}{\text{volume solid}}$	2·28–2·84
Specific gravity	1·30–1·63 (more usually 1·2–1·3)
Thermal expansion, 10^{-5} per °C.	14–16
Thermal conductivity 10^{-4} cal. per sec. cm. °C.	5·3–8·7
Softening point	70°–150°C.
Electrical resistivity (by volume) 30°C., 10^{10} ohm cm.^{3}	6·2
Breakdown voltage, 60 cycle volts per mil.	590–620
Dielectric constant, 60 cycle	7·1–8·4
Power factor, 60 cycle, per cent.	9·1–10·5
Dielectric constant, R.F.	4·3–5·4
Power factor, R.F. per cent.	6·8–10

Additional Data on Unfilled Cellulose Acetate Moulding Powder (from Chem. and Ind. 1936, 55, 36).

Water absorption	1·9% by weight in 48 hours.
Tensile strength	3,500–5,000 lb. per sq. in.
Cross breaking strength	11,000–13,000 lb. per sq. in.
Impact strength	10–15 kg. cm.
Permittivity	Ca 6
Power factor at radio frequencies	0·057-0·059

Comparison of Cellulose Acetate Moulding Powders with Thermosetting Moulding Powders.—The cellulose acetate compositions are permanently fusible and so the scrap can be re-used. There is no curing or baking period so injection moulding can be carried out at a speed of 8 times that of moulding thermosetting resins. The cellulose acetate compositions are more flexible, and withstand rougher treatment. The electrical properties are better than those of phenol-formaldehyde or urea-formaldehyde resins. During ageing there is no change in shape. They can be cemented with acetone. The colours are relatively permanent and free from the yellowing of phenol-formaldehyde powders.

The disadvantages include low softening point—acetate mouldings will not withstand temperatures above 80°–90°C. They are attacked by mild alkalis. They absorb moisture (*see* Tables). They are higher in price, 2*s.* to 4*s.* per lb., but the increased speed of moulding compensates for this in the case of small mouldings.

CELLULOSE ETHER PLASTICS.

Introduction.—The cellulose ethers differ essentially from the esters of cellulose in chemical structure and are more stable, incapable of undergoing hydrolysis, and therefore resistant to acids and alkalis. Films and coatings made from them do not undergo discoloration on exposure to ultra-violet light and like cellulose acetate are relatively non-inflammable. The solubilities of the ethers vary, some being soluble in organic solvents, some dissolving in dilute alkali, and some in water. The solubility of the cellulose ethers varies with the degree of etherification. Ethylcellulose, for example, is soluble in alkalis, water, or organic solvents according to the degree of etherification. The following table summarises the solubilities of some known cellulose ethers, and shows the effect of the degree of etherification.

Approximate Number of Hydroxyl Groups replaced per $C_6H_{10}O_5$.

	Soluble in alkalis.	Soluble in water.	Soluble in organic solvents.
Methyl-cellulose	0·25 (3–4% $—OCH_3$)	1·2–1·5 (22–26% $—OCH_3$)	3 (44–45% $—OCH_3$,
Ethyl-cellulose	0·25 (5% $—OC_2H_5$)	1·2 (27% $—OC_2H_5$)	2·2 (47% $—OC_2H_5$)
Glycol-cellulose	0·25 (3–4% $—OC_2H_4OH$)	—	—
Benzyl-cellulose	—	—	1·8 upwards (59% $—OCH_2{\cdot}C_6H_5$)

The technical applications of these ethers depend on their solubility. The alkali soluble types have outlets in textile finishing. They could also be employed in the same way as viscose (cellulose xanthogenic ester) in the preparation of films, rayon, etc., and have the following advantages over viscose:

(1) Their solutions are more stable.
(2) The products regenerated from alkaline solution require no desulphurising.
(3) The products require no bleaching.
(4) There are no odours during coagulation corresponding to the odours which arise during the conversion of cellulose xanthate to cellulose.
(5) There is no need for careful control and ageing of the solutions, a necessary procedure in the case of the alkaline viscose solution.
(6) When freed from caustic soda they may be stored indefinitely.

Water-soluble cellulose ethers, soluble in cold water and insoluble in hot water, form solutions similar to gum tragacanth, but do not become acid or ferment on storing. They are used industrially as emulsifying agents, fixing agents for printing and thickening agents for textile printing, where they possess advantages over starch and British gum.

The types of ethyl- and benzylcellulose which are soluble in organic solvents have industrial possibilities similar to those of cellulose acetate.

The cellulose ethers, however, are more expensive and so are only employed where their special chemical properties, such as freedom from hydrolysis, make them particularly suitable.

Comparison of the Properties of Cellulose Ethers (Soluble in Organic Solvents) with Cellulose Esters

(1) *Water Resistance.*—The hygroscopicity of certain types of cellulose ethers is low

	72% humidity/ 20°C.	100% humidity/ 20°C
Hygroscopicity.	%	%
Ethylcellulose (47% —OC_2H_5)	2	—
Benzylcellulose	0 9	2 45
Nitrocellulose	2 0	4 6
Cellulose acetate (acetone soluble)	3 6	11 1
	Mg /sq in /hr	
Moisture Permeability.		
Ethylcellulose (47% —OC_2H_5)	2 54	4 39
Benzylcellulose	0 8	1 20
Nitrocellulose	1 15	3 09
Cellulose acetate (acetone soluble)	2 14	5 51

By the addition of suitable plasticisers, wax, etc., the above figures can be reduced still further. These ethers have therefore possibilities in moisture proofing compositions.

(2) *Acid and Alkali Resistance*—Benzylcellulose compositions are unattacked by relatively concentrated acids and alkalis, such as sulphuric acid up to accumulator strength, and caustic soda up to 50% concentration.

(3) *Relative Non-inflammability.*—It must be emphasised that non inflammability is purely a relative term and all cellulose derivatives will burn if the temperature is sufficiently high. The cellulose ethers are relatively non inflammable compared with nitrocellulose and are similar in inflammability to cellulose acetate.

(4) *Thermoplasticity*—The cellulose ethers differ from nitrocellulose which decomposes at higher temperatures and must be treated with care even at 120 C., and in this they again resemble cellulose acetate. This thermoplasticity may be useful in certain cases, for example, heat sealing lacquers.

(5) *Chemical Stability.*—The resistance to the attack of acids and alkalis has already been noted, but the chemical stability of cellulose ethers is evinced in another form, namely, freedom from discoloration on exposure to ultra-violet light. In this they are superior to nitrocellulose and similar to cellulose acetate.

(6) *Specific Gravity.*—The specific gravity of cellulose ethers is in some cases less than that of the esters.

	Specific gravity.
Benzylcellulose	1·2
Ethylcellulose	1·2
Cellulose acetate	1·5
Nitrocellulose	1 55

(7) *Tensile Strength.*—The tensile strengths of films made from some cellulose esters and ethers are as follows :

	Lb per sq in
Benzylcellulose	6,000–7,000
Ethylcellulose	7,000–8,000
Cellulose acetate	8,000–9,000
Nitrocellulose	9,000–11,000

(8) *Cheap Solvents.*—The solvents used for cellulose ethers are of the hydrocarbon type rather than the ester type and therefore inexpensive mixtures can be formulated.

BENZYLCELLULOSE LACQUERS.

Benzylcellulose lacquers and enamels are prepared in the same way as nitrocellulose lacquers and enamels. The benzylcellulose, however, is obtained in the form of a dry pale yellow powder. It is soluble in mixtures (80 : 20 by volume) of aromatic hydrocarbons and alcohol The best method of preparing a solution of benzylcellulose is to wet the granular powder with industrial spirits and then add the aromatic solvent The solution may be made up in any of the types of stirring, shaking, or tumbling apparatus commonly used in paint manufacture In preparing very viscous solutions or dopes, say 30–40% solutions of benzyl cellulose, an apparatus of the Werner Pfleiderer type is the most suitable. The pigments are dispersed in the usual types of grinding or milling machinery There are no restrictions on the type of pigment used

Solvents for Benzylcellulose Hydrocarbons.—Aromatic hydrocarbons such as benzene, toluene, and xylene have a gelatinising effect on benzylcellulose, and excellent solvent mixtures are formed by the addition of 20% of industrial spirits.

Aliphatic hydrocarbons have no solvent action, even when mixed with alcohol, but may be added as diluents to some solutions.

Alcohols.—Aromatic alcohols, *e g* benzyl alcohol, are solvents. Aliphatic alcohols are not themselves solvents, but confer solvent power on aromatic hydrocarbons and on chlorinated solvents

Ethers.—Aromatic ethers and mixed ethers are solvents. Methyl cellosolve (the methyl ether of ethylene glycol) and 1:4-dioxane are solvents. The latter, of course, is generally avoided because of its toxicity.

Ketones—Ketones themselves are non solvents, but the addition of 20–50% benzene confers solvent power in some cases, *e.g.* benzene-acetone (50 : 50 by volume). *Cyclo*hexanone is a solvent.

Esters.—A certain solvent action is possessed by some of the lower fatty esters, but this is improved by the addition of 20% benzene or toluene.

Chlorinated Solvents.—Chlorinated derivatives of ethane and ethylene with the addition of 20% industrial spirits form good solvent mixtures.

Ethylene chlorhydrin and dichlorhydrin are both solvents for benzylcellulose.

Softeners.—The best plasticisers are : tricresyl phosphate, dibutyl phthalate, dicresylin (ditolyl

ether of glycerol). Others include triphenyl phosphate, benzyl benzoate, *p*-toluene sulphanilide, dibenzyl phthalate, butyl stearate. Of these, only benzyl benzoate, dibenzyl phthalate, and dicresylin are solvents at ordinary temperatures. Tricresyl phosphate is a solvent at elevated temperatures.

Chlorinated naphthalenes such as Seekay Wax may be employed as plasticisers but in limited quantity; at 20% and over they tend to crystallise out.

Castor oil may be used as a softener.

The benzylcellulose film is softer and more flexible than either a nitrocellulose or a cellulose acetate film and consequently a smaller proportion of plasticiser is required. 10–15% on the weight of benzylcellulose is generally sufficient in the case of a clear film, while in pigmented films the proportion may be increased to 20%.

The natural resins most suitable with benzylcellulose are dammar and run congo copal.

Benzylcellulose Moulding Powders.

Composition and Method of Manufacture.—The benzylcellulose used in moulding powder manufacture is generally a dibenzyl ether of cellulose, a pale yellow powder with a m.p. of 180°C. Benzylcellulose is more thermoplastic than most cellulose derivatives. No solvent is necessary in incorporating it with fillers, colouring matter, etc., in the preparation of moulding powders.

The quantity of plasticiser used (*see* benzyl cellulose lacquers) depends on the percentage of filler present in the final composition and on the degree of flexibility required in the moulding. The plasticiser content is generally from 4–10% on the weight of benzylcellulose, but may vary above or below this. Tricresyl phosphate helps to maintain the fire-resisting nature of the compositions. The fillers used with benzylcellulose are mineral fillers. The quantity varies, again according to the properties required in the final composition, but the thermoplasticity of the benzylcellulose permits the use of higher quantities than in cellulose acetate moulding powders. The filler content may be even above 50% and the compositions still be easily moulded. The increased proportion of filler means increased specific gravity and an increased weight of powder required for moulding. The fillers used include china clay, blanc fixe, barytes, lithopone, zinc oxide and powdered asbestos. The colouring materials used include inorganic pigments, lakes and dyestuffs.

The moulding powders are manufactured by roughly mixing the benzylcellulose, plasticiser, filler and pigment, and then completing the mixing on hot rolls. When a large percentage of filler is used the bulk of the filler may be added while the benzylcellulose and plasticiser are mixing on the rolls. The incorporation, temperature, and speed of the rolls are similar to those used for the preparatoin of cellulose acetate moulding powders. The crêpe is removed from the rolls, cooled, and ground into granular form.

Moulding.—As in the case of cellulose acetate powders, moulding can be carried out by the compression and by the injection methods. The temperature of the mould in compression moulding is about 110°C., and the pressure is ½–1 ton per sq. in.

In injection moulding the temperature required varies according to the quantity of filler in the powder. Most lightly filled powders mould at temperatures of 130°–140°C. Heavily filled powders may require temperatures of 160°–170°C. These figures refer to the outside temperature of the reservoir or "pot" of the injection press.

Properties.—

Specific gravity	1·2–2·0
Bulk density	0·6–1·0
Tensile strength— . . .	
(*a*) Compression moulded	2,400–3,700 lb. per sq. in.
(*b*) Injection moulded .	3,780–5,520 lb. per sq. in.
Softening point	About 70°C.
Electrical resistivity—	
(Volume) ohms per cm.^{3} .	$2{\cdot}30\text{–}3{\cdot}21 \times 10^{13}$
(Surface) ohms per cm.^{3} .	$2{\cdot}40\text{–}2{\cdot}50 \times 10^{12}$
Breakdown voltage (volts for 0·1 minute)	2,000–5,000
Hygroscopicity (72·5% saturation at 20°C.)—	
After 24 hours . . .	0·40–0·99%
After 48 hours . . .	0·40–1·00%
Exposure in 100% saturated atmosphere; gain in weight	0·19–0·38%
Immersion of benzylcellulose moulding in water—	
Gain in weight after 24 hours (0·0007 – 0·0011 *grains per sq. cm.*) . .	*0·23–0·40%*
Gain in weight after 192 hours (0·0022 – 0·0041 grains per sq. cm.) . .	0·67–1·24%

The outstanding features of benzylcellulose moulding powders are their low hygroscopicity and their resistance to acids and alkalis. Mouldings remain visibly unattacked after 15 months' immersion in various strengths of sulphuric acid: 10% by volume (sp.gr. 1·098), 20%, 30%, 40%, and 60% (sp.gr. 1·5888) at room temperature, 5% hydrochloric acid, and 5% acetic acid do not affect the mouldings.

Alkali Resistance.—Benzylcellulose moulding compositions resist caustic soda solutions of 1–40% strength at room temperature and show remarkable resistance to alkaline solutions at higher temperatures.

Benzylcellulose mouldings also resist various aqueous inorganic solutions. (*N*/10 potassium permanganate, 26% solution sodium thiosulphate, 5% sodium sulphide, saturated solutions of zinc chloride, potassium chlorate and potassium iodide) for 8 weeks. A series of tests carried out shows that ink resistance is very good, and the powders are therefore useful in fountain pen manufacture.

Trade Names.

A. T. Cellulose, Ethylcellulose (*see* Cellulose Ether Plastics).

Bexoid	A non-inflammable or safety celluloid made from cellulose acetate (*see* Cellulose Ester Plastics).
Celastoid	A non inflammable or safety celluloid made from cellulose acetate (*see* Cellulose Ester Plastics).
Cellastine	A thermoplastic moulding powder made from cellulose acetate (*see* Cellulose Ester Plastics).
Cellomold	A thermoplastic moulding powder made from cellulose acetate (*see* Cellulose Ester Plastics).
Coblac	Pigmented celluloid like flakes used for enamel manufacture (*see* Cellulose Ester Plastics).
Colloresin	Methylcellulose (*see* Cellulose Ether Plastics).
Fiberloid	Nitrocellulose-camphor celluloid (*see* Cellulose Ester Plastics).
Globlak	A variety of highly pigmented black nitrocellulose flakes used for enamel manufacture (*see* Cellulose Ester Plastics).
Glutolin	Methylcellulose (*see* Cellulose Ether Plastics).
Plastacele	Cellulose acetate celluloid (*see* Cellulose Ester Plastics)
Pyralin	Nitrocellulose-camphor celluloid (*see* Cellulose Ester Plastics).
Rhodoid	A cellulose acetate moulding powder. A cellulose acetate celluloid is sold under the same name (*see* Cellulose Ester Plastics)
Rhodophane	Cellulose acetate films (*see* Cellulose Ester Plastics).
Sicoid	Cellulose acetate celluloid (*see* Cellulose Ester Plastics).
Tylose	Methylcellulose (*see* Cellulose Ether Plastics)
Xylonite	Nitrocellulose–camphor celluloid.

D. T.

CELTIUM. Urbain first detected, by optical and magnetic observation, the existence of a white earth having properties intermediate between those of lutecia and scandia, and named the substance celtia or celtium oxide, Ct_2O_3. Coster and Hevesy (Nature, 1923, 111, 79), examining the X-ray spectra of a number of minerals, detected six lines which they attributed to the element of atomic number 72, and named hafnium, stating that celtium was probably the same element. Urbain and Dauvillier (Nature, 1923, 111, 218), asserted that the lines observed by them were identical with those observed by Coster and Hevesy, and claimed priority for the name celtium. The controversy continued (Dauvillier, Compt. rend 1923, 176, 676; De Broglie and Cabrera, *ibid.* p. 433; Urbain, Chem. and Ind. 1923, 42, 764; Brauner, *ibid.* p. 884; Hansen and Werner, Nature, 1923, 111, 461; Coster and Hevesy, *ibid.* p. 462; King, *ibid.* 1923, 112, 9), but the name hafnium is now generally accepted for the element.

CEMENT *v.* BUILDING MATERIALS.

CEMENTITE, an iron carbide, Fe_3C, containing 6 9% carbon, is an important constituent of cast iron and steel (Abel and Deering, Proc. Inst. Mech. Eng 1885, 30; Moissan, Compt. rend 1896, 122, 421) In steels containing 1 5% or more of carbon, free cementite is found crystallised in large pseudo hexagonal plates (Groth, Chem. Krystallographie, 1906, i), and in practically all steels it exists with pure iron (*ferrite*), in the eutectic mixture called *pearlite* (Ledebur, Stahl u. Eisen, 1898, 18, 742).

It is very brittle and harder than hardened steel or glass (H =6) (Muller, Stahl u. Eisen, 1898, 18, 292), and its presence is the cause of the hardness of "white" or "chilled" cast iron (Howe, Metallographist, 1901, 177). It is recognised under the microscope by its hardness and resistance to etching

As *cohenite*, it is present in meteorites (Weinschenk, Ann Museum, Wien, 1889, 4, 94).

CENTAURY, CENTAUREA. *Cnicus benedictus*, Fam Gentianaceæ, Blessed Thistle, contains the bitter tonic *cnicin*, $C_{42}H_{56}O_{15}$.

CENTRALITES. These are derivatives of urea which are employed in the manufacture of smokeless powders to assist in the gelatinisation of the nitrocellulose and also to act as stabilisers of the powders during storage Centralite 1 consists of diethyldiphenylurea, Centralite 2 is dimethyldiphenylurea, and Centralite 3 is ethylmethyldiphenylurea. Of these, Centralite 1 is used to a much greater extent than either of the other two varieties H S.

CEPHAELINE. Cephaeline was named and first characterised by Paul and Cownley (Pharm J. 1894, [iii], 25, 111), who showed that the ether soluble alkaloids of ipecacuanha could be separated into phenolic and non-phenolic fractions. The chief constituent of the phenolic fraction is cephaeline, and that of the non-phenolic fraction emetine, which Carr and Pyman showed later (J.C S. 1914, 105, 1591) to be cephaeline mono-methyl ether.

Patents have been taken out by the following for the preparation of emetine by the methylation of cephaeline; by H. S. Wellcome, F. H. Carr, and F. L. Pyman, B.P. 14677 and 17483 (1913) by means of dimethyl sulphate and sodium methyl sulphate respectively; by Farbw. vorm. Meister, Lucius und Bruning, G.P. 298678 (1916) by means of diazomethane, by Chem. Fabr. vorm. Sandoz, B.P. 291088 (1928) by means of phenyltrimethylammonium hydroxide; by J. W. Meader, B.P. 11717, 11718, 11719 (1915); 103881, 104052, 105722 (1916); U.S.P. 1209575 (1917); and by Farbw. vorm. Meister, Lucius und Brüning, G.P. 301498 (1915) for the preparation of homologues of emetine by the alkylation of cephaeline with derivatives of alcohols other than methyl alcohol.

Properties.—Cephaeline and its salts have been fully described by Carr and Pyman (*l c.*). It has the formula, $C_{28}H_{38}O_4N_2$, and contains one phenolic hydroxyl group, three methoxyl groups, one tertiary nitrogen atom common to two rings, and one secondary nitrogen atom contained in a ring. A probable constitutional

formula for cephaeline has been put forward by Brindley and Pyman (J.C.S. 1927, 1067).

Cephaeline forms colourless needles from ether, melting at 115°–116° (corr.), $[\alpha]_D$ −43° in chloroform (c=2), sparingly soluble in water, ether, or light petroleum, easily so in alcohol or chloroform. The hydrochloride $B,2HCl,5$ to $7H_2O$ *forms colourless prisms, easily soluble in* water, melts at 245°–270° (corr.) when anhydrous, *and is dextrorotatory.* The hydrobromide is also crystalline. F. L. P.

CEPHALANTHIN, $C_{22}H_{34}O_6$, m.p. 181° $[\alpha]_D$ +20·2°, a bitter stuff from the bark of *Cephalanthus occidentalis.* On hydrolysis it yields a sugar which is either glucose or galactose (Claassen, Pharm. Ztg. 1889, 34, 384). E. F. A.

CEPHARANTHINE, $C_{37}H_{38}O_6N_2$, m.p. 140°–145°, $[\alpha]_D^{21}$ +204°, is an amorphous slightly yellow base which was found by Kondo, Yamashita and Keimatsu (Chem. Zentr. 1934, II, 3256) in the roots of *Stephania cepharantha* Hayata (Fam. Menispermaceæ) together with the alkaloid *iso*tetrandrine. The alkaloid is a tertiary, non-phenolic base, it contains three OMe and two NMe but no alcoholic OH groups; the three remaining oxygen atoms probably represent O-bridges. Apparently cepharanthine does not contain double bonds; it reduces ammoniacal silver nitrate but not Fehling's solution. It is soluble in organic solvents except light petroleum; for colour reactions consult Kondo *et al.* (*l.c.*). It forms amorphous salts with 2 mols. of acid, *e.g.* picrate, oxalate, perchlorate, and chloroaurate.

The first step of the Hofmann degradation *yielded one crystalline methin base (α'-methine),* $C_{39}H_{42}O_6N_2$, optically inactive, m.p. 170°–171°, prisms and plates, giving a crystalline methiodide) and two amorphous methin bases (*α-methine*, $C_{39}H_{42}O_6N_2$, optically inactive, m.p. 143°, yellow, giving a crystalline methiodide and methosulphate, and *β-methine* (no details known)).

The α-methine base is identical with phaeanthine-methine A (Santos, Ber. 1932, 65, [B], 474), although cepharanthine and phaeanthine are different. Ozonisation of α-cepharanthine-methylmethine gave the 6-methoxy-diphenyl-ether-3:4'-dialdehyde identical with that obtained by ozonisation of tetrandrine and trilobine, and a base which yielded a yellow crystalline methiodide, $C_{26}H_{38}O_6N_2I_2$+H_2O, m.p. 217°, (Kondo and Keimatsu, Amer. Chem. Abstr. 1935, 29, 7988). Although the constitution of cepharanthine is still unknown, the above results point to the fact that it belongs to the bis-coclaurine alkaloids (for a survey, *cf.* Kondo, Arch. Pharm. 1936, 274, 65). Schl.

CERADIA. The product of *Ceradia* (*Othonna*) *furcata* Lindl. It is an amber-coloured oleo-resin with the odour of elemi (R. Thomson, Phil. Mag. 1846, [iii], 28, 422).

CERALUMIN *v.* ALLOYS, LIGHT.

CERARGYRITE or HORNSILVER. Native silver haloids, Ag(Cl,Br,I), occurring as small holohedral-cubic crystals and as compact masses with a horny appearance and texture. The material is soft (H.=2½), tough, and sectile, and cuts like horn. On exposure to light, it quickly darkens. The name "hornsilber" was used by C. Gesner in 1565, and the Greek form cerargyrite was first used by F. S. Beudant in 1832. After the recognition of the bromide and chlorobromide in 1841 and 1842, the name cerargyrite came to be applied more especially to the chloride. But as the different members of the group so closely resemble one another that that they can often only be distinguished by analysis, it is more expedient to include them as sub-species under the name cerargyrite (*see* Prior and Spencer, Min. Mag. 1902, 13, 174), viz.:

Chlorargyrite, AgCl.	Grey or colourless, sp.gr. 5·556.
Bromargyrite, AgBr.	Greenish-grey.
Embolite, Ag(Cl,Br).	Greenish-grey.
Iodembolite, Ag(Cl,Br,I).	Greenish-yellow to orange-yellow.

Isomorphous mixtures are the rule, and of these sub-species *embolite*, with chlorine and bromine in indefinite proportions, is the most abundant. Large quantities of these minerals have been mined as silver ores in Mexico, Chañarcillo in Chile, and Broken Hill in New South Wales. They occur in the upper oxidised zones of veins of silver ore, and have no doubt been formed by the action of salt waters percolating from above.

Silver iodide forms a distinct mineral, *iodyrite*, crystallising in the hexagonal system, but at a temperature of 146° it passes over into a cubic modification. L. J. S.

CERASIN. The insoluble constituent of cherry tree gum.

CERBERIN, $C_{27}H_{40}O_8$, m.p. 191°, $[\alpha]_D$ −74·8°, is the glucoside of the seeds of *Cerbera odollam.* It is hydrolysed to glucose and cerberetin (De Vry, Ber. K. Akad. Wien, 1864, Jan. 16) (*v.* CARDIAC GLYCOSIDES). E. F. A.

CEREALS.

MAIZE.—*Zea Mays* Linn.; Indian corn.

This cereal has been cultivated from prehistoric times in North and South America, and is now widespread, its production being little short of that of wheat. It requires a dry, hot climate. Many varieties are known, white maize being favoured for human food in Europe and South Africa, yellow in America. The yield of the crop is high.

The composition of maize varies less than that of wheat. It is remarkable for its high fat content, about equal to that of oats. Analysis of an average mixed American maize gave:

Moisture. %	Oil. %	Protein. %	Digestible carbohydrate. %	Fibre. %	Ash. %
12·55	4·37	10·62	69·71	1·50	1·25

(Milling, 1933, 80, 231; 81, 513). The characteristic protein is *zein*, more abundant in the outer layers than in the endosperm; *myosin*, *vitellin*, another globulin, and small quantities of two albumins have also been isolated from maize. The protein content is affected by climate and especially by rainfall.

During ripening, globulin and glutenin increase at a uniform rate; zein, at first present in small quantity, is formed rapidly as maturity approaches. An accompanying decrease in water-soluble non-protein nitrogen indicates the synthesis of zein from simpler amino compounds. The biuret reaction gives a reddish-violet coloration, which can be used to detect and estimate maize in the presence of wheat (Czyzewsky, Z. ges. Getreide- u. Mühlenwes 1932, 19, 141). The principal carbohydrate present is starch, particularly plentiful in the hard grained varieties; soft-grained varieties are richer in fat (Dvorak, Mezögazdasagi Kutatások, 1935, 8, 156; Muhlenlab. 1935, 5, 110). Less than 1% of sucrose is present with a small amount of reducing sugar, also dextrin and furfuroids and pentosans up to about 5%. The fats (72% fluid, 28% solid) constitute about 28% of the embryo The latter is removed whole in milling, in order that the flour shall not be rendered dangerous as a foodstuff by the oil turning rancid; modern maize flour is almost completely free from oil Rancidity is promoted by spontaneous heating, and is suppressed by keeping the moisture content below 15%; it can be measured by the acidity of an alcoholic extract (Milling, 1933, 80 231; Mühle, 1935, 72, 35). Maize contains 0 1–0 2% of sulphur, mainly associated with the protein; phosphorus is present as phytin from after pollination till early in germination (de Turk, Holbert, and Howke, J. Agric. Res 1933, 46, 121). The mineral content of the grain depends on soil conditions, fertilisation, and rainfall; tables are given by Wolff, "Aschenanalysen"; Bertrand and Mokragnatz (Bull Soc. chim. 1925, iv, 37, 554); and Schrumpf Pierron (Compt. rend Soc Biol. 1932, 109, 699) The vitamin content is also variable, vitamin A is present, mainly in the outer part of the endosperm, associated with the yellow colour (Meyer, J. Agric. Res 1929, 39, 767; Hauge and Trost, J. Biol Chem. 1928, 80, 107, 1930, 86, 161, 167; Mangelsdorf and Fraps, Science, 1931, 73, 241), but is gradually lost on storage (Fraps and Treichler, Ind Eng Chem. 1933, 25, 465). Vitamin D is lacking Maize supplies sufficient vitamin E when it forms 20% of the diet. The use of maize, especially white maize, as human food is associated with pellagra, but the nature of the connection is not clear It has been attributed to unsound grain, and to the absence of lysin and tryptophan from the hydrolysis products of zein. Pellagra is prevented by foodstuffs containing vitamin B_2, but as this vitamin is also present in maize its deficiency cannot be the sole cause of the disease Possibly some toxic substance is responsible (Aykroyd, Nutr. Abs. 1933, 3, 337; "Vitamins," Med. Res. Counc. 1932, p. 184).

Maize is largely used for feeding animals and poultry. The nutritive value of the whole grain is slightly inferior to that of wheat (Boas-Fixsen, Hutchinson, and Jackson, Biochem. J 1934, 28, 592), the protein being equal (Fixsen and Jackson, Biochem. J. 1932, 26, 1919, 1923; 1934, 28, 592) and the germ inferior (Biscaro and de Caro, Quad. Nutrizione, 1935, 2, 189) Its digestibility is second only to that of wheat. Its large oil content being detrimental to the fat of pigs, degermed meal is used for pig feeding (Woodman and Evans, J. Agric. Sci 1932, 22, 670). The germ is used for poultry food and in the manufacture of oil for soap, margarine, baking, salad oil, and stand oil for paints (Wilborn, Farben Ztg. 1926, 32, 240). Alcoholic drinks are made from maize, and a large variety of manufactured products, the chief being starch, gluten feeds, corn syrup, and dextrin. The fermentation of the stalks and cobs gives acetone, a gas and a residue suitable for paper making (Boruff and Buswell, Ind. Eng. Chem. 1929, 21, 1181, 1930, 22, 931). Furfuraldehyde, and various perfumes, insecticides, etc., can also be obtained (Govier, Amer. Miller, 1935, 63, (1), 90) E. A F.

MILLET

Millet is a name applied to a number of species of grasses belonging principally to the Families Andropogoneæ and Paniceæ, important as food for man and forage for cattle, particularly in India.

Andropogoneæ.—A. Sorghum (great millet, sorghum, cholam, jawar (dari), broom corn, sugar sorghum, Kaffir corn, durrha, milo maize) The term "sorghums" includes many varieties of the species which have been known at various times as *Andropogon Sorghum* or *Sorghum vulgare*

Paniceæ Panicum.—P. miliaceum (Linn) (common millet, Indian millet, ragi, marua, Proso hog millet, Indian buffalo grass)

P miliare Lam (little millet)

P texanum Vasey (Texas millet or Colorado grass)

P frumentaceum Roxb (Sauwa millet Shamaeo, Deccan grass).

P maximum Jacq (Guinea grass)

P. decompositum (Australian millet)

P sanguinale Linn (Polish millet)

P Crus galli Linn. (Japanese broom corn).

Pennisetum —P. typhoideum Rich (pearl millet, Egyptian, or cat's tail millet, bajri).

Setaria —S italica Beauv. (golden or Italian millet), varieties of this constitute German millet or Hungarian grass, Japanese millet, Boer manna, and California green molia

Other millets are · *Paspalum scrobiculatum* Linn (Koda or Kodon millet), *Eleusine coracana* (African millet)

The importance of the millets may be gauged from the following figures, taken from the "I.I.A Yearbook of Agricultural Statistics" (1934–1935)

India (including Native States)

	Hectares
Millet—ragi or marua (*Panicum miliaceum*)	2,694,098
Pearl millet—bajri or cumbu (*Pennisetum typhoideum*)	8,261,521
Sorghum—cholam or jawar (dari) (*Andropogon Sorghum*)	14,667,445

United States of America.

Sorghum (grain)	1,213,000
Sorghum for forage—	
(a) Grain	1,850,000
(b) Sweet	1,439,000

South Africa.

	Hectares.
Millet (Boer manna) (*Setaria italica*)	11,344
Sorghum (Kaffir corn)	87,118

Proximate Analysis.—The following analyses ("Food grains of India," Church, 1886 and 1891) will serve to show the composition of the seeds of many "millets."

Species.	Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Crude ash. %
Sorghum vulgare	12·5	9·3	2·0	72·3	2·2	1·7
Sorghum vulgare	13·2	9·3	3·3	68·0	2·5	1·7
Var. *saccharatus*	12·8	11·8	3·0	68·3	3·0	1·1
Pennisetum typhoideum .	11·3	10·4	3·3	71·5	1·5	2·0
Setaria italica .	10·2	10·8	2·9	73·4	1·5	1·2
Panicum—						
miliare . .	10·2	9·1	3·6	69·0	4·6	3·5
miliaceum .	12·0	12·6	3·6	69·4	1·0	1·4
frumentaceum[1]	12·0	8·4	3·0	72·5	2·2	1·9
sanguinale .	13·4	14·9	4·1	64·5	1·1	2·0
Paspalum scrobiculatum	11·7	7·0	2·1	77·2	0·7	1·3
Eleusine coracana . . .	13·2	7·3	1·5	73·2	2·5	2·3
Rangoon millet	12·4	10·6	3·1	70·3	1·4	2·2
Millet . . .	12·9	11·1	4·5	59·5	7·5	4·5
Dhurra . . .	11·5	9·0	3·8	70·1	3·6	2·0
Pearl millet .	9·2	12·9	5·1	68·5	2·1	2·2

[1] With husk.

Sorghum.

The following tables give the proximate analysis of the different varieties of sorghum, by various authorities, extracted from Winton, "Structure and Composition of Foods," Vol. I, 1934.

Composition of Varieties of Sorghum.

1. *Chamberlain.*

(U.S. Dept. Agric. Bur. Chem. 1909, Bull. 120.)

	Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Ash. %
Edra	10·91	11·44	4·34	80·31	1·73	2·18
Gidjep-jawar .	11·02	10·13	3·30	83 36	1·57	1·64
Davdi-jawar. .	11·35	8·87	2·41	85·31	1·66	1·75
Natal. . . .	10·91	14·30	2·97	78·99	1·94	1·60
Djuggara . .	11·35	13·81	3·52	79·96	1·66	2·04
White milo-maize . . .	12·80	11·12	2·65	82·44	2·12	1·67
White Kaffir corn	12·10	12·94	2·82	79·95	2·32	1·97
White Kaffir corn	12·55	11·56	3·33	81·68	1·78	1·65
Red Kaffir corn .	12·31	10·06	3·73	83·13	1·56	1·51
Dwarf milo maize	11·84	12·69	3·41	80·71	1·65	1·34

2. *Bale and Rothgeb.*

(U.S. Dept. Agric. 1915, Farmers Bull. 686.)

		Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Ash. %
Milo maize .	67	9·32	12·54	3·15	71·89	1·48	1·62
Dwarf milo maize . .	55	9 38	12·16	3·27	72·09	1·47	1·63
Feterita . .	8	9·58	14 00	2·90	70·32	1·48	1·72
Blackhull Kaffir corn	78	9·58	14 10	3 47	69·49	1·58	1·78
Dwarf Kaffir corn . .	13	9 95	13·09	3 25	70 49	1·52	1·70
Red Kaffir corn . .	37	9·56	12·01	3·16	72·03	1·51	1·73
Shallu . .	10	10·38	15 17	3 69	68 86	1·92	1·98

3. *Winton.*

(Conn. Agric. Exp. Sta. Ann. Rep. 1902, 338.)

	Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Ash. %
Broom Corn[1]						
Long brush evergreen .	12·63	10·19	3·49	67·90	2·83	2·46
Early Japan .	12·32	11·87	3·52	65·56	3·84	2·89
California Golden . .	12·86	10·44	3·74	65·54	3·84	3·28
Improved dwarf . .	12·88	9·56	3·20	64·93	6·19	3·24
Sugar Sorghum[1]						
Early amber .	12·37	11·12	3·74	67·43	3·08	2·26
Early orange .	13·00	9·81	3·65	69·80	1·99	1·75
White Kaffir corn[2] . . .	12·66	10·31	3·30	71·01	1·44	1·28
Red Kaffir corn[2]	12·23	10·62	3·11	71·42	1·10	1·19
White dwarf[2] .	12·20	12·62	3·95	67·63	1·53	2·07
Brown dwarf[2] .	12·48	12·25	3·97	68·45	1·19	1·66
White milo maize[2] . .	11·98	11·19	3·17	70·92	1·37	1·37
Yellow milo maize[2] . . .	11·18	10·31	2·91	72·08	1·75	1·77

[1] With chaff. [2] Without chaff.

4. *Bidwell and others.*

(U.S. Dept. Agric. Bull. 1922, 1129.)

Kernels.	Ash. %	Ether extract. %	Protein. %	Crude fibre. %	N-free extract. %	Starch. %	Pentosans. %
Kaffir . .	1·80	4·10	12·70	1·80	79·60	61·90	3·30
Milo . .	1·89	3·47	13·99	1·93	78·72	68·52	3·95
Feterita .	*1·79*	*3·06*	*16·69*	*2·22*	*76·24*	*64·16*	*3·38*

5. *Baird and Francis.*

(Ind. Eng. Chem. 1910, 2, 531.)

Summary of 5 Analyses.

Kaffir Corn.	Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Ash. %
Minimum . .	11·26	11·37	3·46	65·33	1·88	1·20
Maximum . .	13·45	12·85	3·80	70·83	2·90	1·67
Average. . .	12·36	12·11	3·63	68·08	2·39	1·43

The various millets are largely used as fodder plants, but cases of death among animals fed upon young plants (of sorghum in particular) have been numerous. It has been shown by Dunstan and Henry (Phil. Trans. 1902, A. 399) that the young leaves and shoots of *Sorghum vulgare* contain a glucoside, dhurrin, which readily hydrolyses by the action of an enzyme also present in the plant, yielding *p*-hydroxybenzaldehyde, *d*-glucose, and hydrocyanic acid. These observations were confirmed by Leather in India (Agric. J. India, 1906, 1, part III, 220–225). Brunnich (J.C.S. 1903, 83, 788) obtained as much as 2·44 grains of hydrocyanic acid from 1 lb. of green sorghum at 5 weeks old, corresponding to 13·38 grains per 1 lb. of dry matter. The amount rapidly diminished as the plant grew: At 9 weeks old, the same sorghum yielded only 0·20 grain per 1 lb. of green material (0·76 grain HCN per 1 lb. dry matter).

Willaman (J. Biol. Chem. 1917, 29, 25) states that hydrocyanic acid is present in sorghum not only as the glucoside dhurrin but in another form. He also finds that leaves subjected to a low temperature contain more hydrocyanic acid in both forms than ordinary leaves, thus

explaining and confirming the general opinion that young sorghum is especially poisonous after a frost.

Dowell (J. Agric. Res. 1919, 16, 175) found that sorghum cut after a drought contained 0·0514% HCN, whereas that grown under normal conditions contained only 0·0220%.

Pinckney (J. Agric. Res. 1924, 27, 717) reported that the application of nitrates increased the HCN content of the plant. Tsukunaga (Agric. Exp. Sta Manchurian Rly. Co. Res. Bull. 1931, No. 2) found that the leaves of sorghum contained 0·0358–0·1066% HCN and records variations associated with seed colour.

Acharya (Indian J Agric. Sci 1933, 3, 851) has studied in detail the development of HCN in cholam (sorghum).

The HCN is best determined by permitting the auto enzymic decomposition of cyanogenetic substances in H_2O extracts of macerated material (48 hours) with subsequent distillation and determination of HCN by customary methods Addition of $CHCl_3$ or toluene to extracts, as a preservative, does not check the action of the enzyme. The HCN content of cholam in the early stages of growth is high and declines steadily to a minimum at the flowering stage. High values occur in droughted plants and secondary growths Leaves contain more HCN than stems or roots. The total HCN and the percentage in dry matter are low in the early morning, rising to a maximum at approximately 2 p m. and declining rapidly after 6 p m. Seedlings grown in darkness have as much HCN as those grown in light. Drying cut plants in the sun reduces their HCN content by 30–40% and in the shade by 10%. Heating at 100° for several hours or brief immersion in 10% aqueous H_2SO_4 destroys the cyanophoric substance, and only traces of HCN remained in plants after ensilage for 2 months. Poisonous plants are detected by means of the starch accumulation in the stems. Acharya's work confirms that of Willaman in that the presence in cholam of CN substances in forms other than glucosides is indicated.

Brunnich (l c) was also able to detect hydrocyanic acid in several other varieties of millet. Tsukunaga (*l c.*) confirmed this.

When sufficiently grown, however, the various millets afford good fodder, and the smaller varieties nutritious and palatable hay. The following are analyses of some millet hays grown in the Transvaal :

	Water %	Protein. %	Fat %	N free extract %	Crude fibre. %	Ash %
Boer manna .	7·2	4·9	1·5	43·0	36·5	6·9
Golden millet	7·9	11·1	1·0	29·5	41·0	9·5
Californian green moba . .	8·0	10·5	1·2	35·6	35·6	9·3
Japan broom corn . . .	9·6	6·8	1·2	33·8	34·8	8·8

Proteins.—The principal protein of Kaffir corn and doubtless of allied if not all varieties of the species is *kaffirin*, a prolamine, first isolated by Johns and Brewster (J. Biol. Chem. 1916, 28, 59), constituting more than half of the protein of the grain. It is similar in ultimate composition to *zein*, of maize, but differs in its decomposition products and certain physical characters. From a 70% alcohol solution, in which it is less soluble than zein, it readily coagulates on overheating.

The ultimate composition of kaffirin as obtained by Johns and Brewster is as follows :

	%
Carbon	55·19
Hydrogen . . .	7·36
Nitrogen	*16·44*
Sulphur . . .	0·60
Oxygen	20·41

Amino Acids of Kaffirin.—Hydrolysis by Jones and Johns (J. Biol. Chem. 1918, 36, 323) yielded the following . glycocol none, alanine 8·08, valine 4·26, leucine 15·44, cystine 0·84, aspartic acid 2·27, glutamic acid 21·23, tyrosine 5·49, phenylalanine 2·34, proline 7·8, tryptophane present, arginine 1·59, lysine 0·95, histidine 1·12, and ammonia 3·46% Total 74·87%.

Narayana and Norris (J. Indian Inst. Sci. 1928, 11A, 94, Table 4) in comparing eleusinin (*v. infra*, p 488) with kaffirin and *sorghumin give the nitrogen distribution as* follows

	Kaffirin from *A Sorghum* [1]	Sorghumin *Sorghum vulgare* [1]
Amide .	20·76	18·96
Humin.	1·35	3·08
Arginine	3·92	4·83
Histidine	1·71	1·19
Cystine	1·23	0·92
Lysine	2·48	3·45
Amino .	68·85	60·01
Non-amino . .	0·32	5·33

[1] Expressed as percentages of total nitrogen.

Jones, Gersdorff and Moeller (J. Biol. Chem. 1924, 62, 183) obtained the following figures in two preparations :

	I %	*II* %
Cystine	0·55	0·53
Tryptophane . .	1·17	0·73

Nitrogen Distribution in Kaffir Corn Protein.—Dowell and Menaul (J. Biol. Chem. 1921, 46, 437) obtained practically all the protein matter of the grain by extracting with dilute alkali and precipitating with acetic acid.

Determinations in this material by Van Slyke's method gave the following results :

Nitrogen as:	%
Humin adsorbed by lime . . } Humin in amyl alcohol extract }	4·40
Cystine	0·96
Arginine	2·41
Lysine	1·05
Histidine	1·78
Amino in filtrate	74·95
Non amino in filtrate . . .	7·20
Amide	8·46

FAT OF MILLETS AND SORGHUMS.—Analyses by Bersch (Landw. Versuchs-Stat. 1895, 46, 103):

	Sap. no.	Iodine no.
Rough millet . .	216	60
Bran	213–216	58–59
Polish	210–212	58
Decorticated . .	213–214	56–61

Smith and Waller (Analyst, 1933, 58, 319) give the characteristics of three specimens of millet oil from *Panicum miliaceum* and of the fatty acids and unsaponifiable matter extracted from the oil.

TABLE I.—PHYSICAL AND CHEMICAL CHARACTERISTICS OF MILLET OIL.

	I. 1930 crop.	II. 1931 crop.	III. 1931 crop.	Bersch, 1895.	Fabris & Settimj, 1907.	Dunbar & Binnewies, 1920.	Koryo oil Japan, 1930.
Sp.gr. at 25°/25°C. . . .	0·9076	0·9194	0·9120	—	0·9275 (15°C.)	0·9228 (22·5°C.)	0·9206 (20°C.)
Refractive index, n_D^{40} . .	1·4620	1·4664	1·4648	—	—	—	1·4649
Saponification value . .	166·8	182·8	183·8	216	183·8	181·5	183·0
Acidity (as oleic), per cent.	31·9	36·6	43·1	—	—	11·9	20
Acetyl value	18·0	—	—	—	—	39·2	—
Unsap. matter, per cent. .	4·9	3·1	4·4	—	—	2·5	5·4
Iodine value (Wijs) . .	132·2	129·1	130·5	60	130·4	92·3 (Hübl.)	114
Bromine value	—	85·5	80·2	—	—	—	—
Calculated iodine value .	—	134·9	127·2	—	—	195·5	—
Neutralisation value of fatty acids	197·8	198·6	198·6	—	—	—	—
Iodine value of unsaponifiable matter	—	—	143·4	—	—	—	—

TABLE II.—FATTY ACIDS EXTRACTED FROM MILLET OIL.

	I. 1930 crop.	II. 1931 crop.	III. 1931 crop.	Fabris & Settimj, 1907.	Dunbar & Binnewies, 1920.	Koryo oil.
Appearance		Liquid with slight crystalline deposit				
M.p. (capillary tube method) .	—	23°–24°C.	22°–23°C.	26°–27°C.	—	—
Iodine value.	—	136·8	96·6	—	—	—
Bromine value	—	85·9	87·2	—	—	—
Calculated iodine value . .	—	136·3	138·4	—	—	—
Thiocyanogen value (15 hours)	—	78·6	77	—	—	—
Calculated composition, per cent.—						
Oleic acid	—	22·7	17·4	—	—	—
Linolic acid	—	64·2	67·8	—	—	—
Saturated acids	—	13·0	14·0	—	—	—
Lead salt and alcohol separation—						
Solid acids, per cent. . .	—	7·0	6·6	15·5	14·7	28·4
Iodine value	—	2·6	2·7	—	24·4	13·1
Liquid acids, per cent. . .	—	93·3	93·4	84·5	85·3	71·6
Iodine value	—	128·1	127·6	146·3	123·8	120·0

The unsaponifiable matter consists largely of a substance (m.p. 285°C.) composed of C 84·5%, H 11·8%, and O 3·7%. This is probably identical with the "Panicol" of Kassner (1888) and "Prosol" of Dunbar and Binnewies (J. Amer. Chem. Soc. 1920, 42, 658). A chloroform solution gives no coloration with sulphuric acid. The Liebermann-Burchard test results in the slow development of a violet tint. The oil contains no vitamin A. Smith and Waller agree with the suggestion of Dunbar and Binnewies that the saturated acids consist of a large amount of palmitic acid and smaller amounts of carnaubic and daturic acids. The unsaturated acids consist of oleic, linolic, and *iso*linolic acids. Winton (p. 113) tabulates analyses of Kaffir corn oil by Baird and Francis (Ind. Eng. Chem. 1910, 2, 531) and of feterita

and milo oil by Francis and Friedemann (Oklahoma Agric. Exp. Sta. 1917, Bull. 117):

Source of oil.	Sp gr.	Ref ind.	M p. °C.	Maumené no.	Sapon. no.	Iodine. no.
Kaffir corn	0·9398	1 4669	44 2	68 1	193 6	109 7
Feterita	0·9260	1 4651	44 7	—	187 3	—
Milo maize	0 9275	1 4675	42 9	—	189·5	—

Source of oil	Reichert-Meissl no	Hehner no.	Acetyl no	Fatty acids titer °C	Unsap matter %
Kaffir corn	4 3	93 2[1]	42 3	34 0	1 72
Feterita .	3 0	95 1	26 8	30 6	0 84
Milo maize	1 3	91 6	20 4	29 7	0·05

[1] Soluble acids 0 66, liquid acids 85 98, solid acid 7 48, and free fatty acids 27 02%.

In most respects the characteristics of the fats of the three sorghums agree closely with each other. Ueno and Kuzei (J Soc. Chem Ind Japan, 1930, 33, 452) obtained from Manchurian grain *Sorghum vulgare*, 3% of a pleasant smelling, brown, pasty oil (Koryo Oil), constants as in Table I.

The yellow-brown fatty acids deposited a small amount of solid acids at 16° and had saponification value 197, iodine value 119 5, the liquid fatty acids (71 6%) and solid acids (28 4%), m p. 53 9°–54 6°, separated by the lead salt–ether method, had respective iodine values 120, 13 1; saponification values 193 7, 215 3. After acetylation the unsaponifiable matter yielded 7·95% of a hydrocarbon (m.p 60 5°–61 8°), steryl acetates (m p. about 64°) and 19 6% of a fraction crystallising at 31 5° having acetyl value 104 2, and containing higher aliphatic alcohols

The unsaturated fatty acids consisted of oleic and lineoleic acids, 2 . 1, and the saturated acids mainly of palmitic acids. Steger and van Loon (Rec. trav. chim 1934, 53, 41) obtained a fatty oil from *Panicum miliaceum* which contained 3 3% of unsaponifiable matter and 88·7% of fatty acids, comprising saturated acids 10 7%, oleic acid 23 9%, linoleic acid 46 9%, linolenic acid 7 2%.

Carbohydrates (Kaffir corn).—Baird and Francis (*l.c.*).

	Starch. %	Pentosans %	Galactans %	Glucose %	Sucrose. %	N free extract %
Minimum .	57 12	3 79	0 10	1 34	0 27	66 16
Maximum .	60 71	5 04	0 24	1 44	0 80	68 44
Average .	58 86	4 33	0 15	1 38	0 53	67 33

Enzymes —Bidwell *et al* (*l c.*) record malting experiments with the kernels of the grain sorghums, milo and feterita, comparing the results with those obtained from Kaffir corn and maize. They do not consider the kernels suitable for malting purposes. The protein content of feterita is higher than that of the other grains. The horny endosperm in each case has more protein than the starchy endosperm. The germs of the sorghums are very similar in composition.

The amylase of cholam (*Sorghum vulgare*) has been studied and compared with that of sprouted barley by Patwardhan and Norris (J. Indian Inst. Sci. 1928, 11, A, 121) and Narayanamurti and Norris (J. Indian Inst. Sci. 1928, 11, A, 134).

There is marked difference in the fat contents of the malts. Cholam contains 4 1% of fat, mainly fatty acids, whereas barley contains 2%, mainly neutral fat. The high fat content of cholam tends to reduce the amount of extract obtainable from the malt.

Cholam amylase is more active in its liquefying power than barley amylase, but the reverse is true of its saccharifying power; hence it is believed that the enzymes are not the same in the two grains.

By the action of cholam amylase on potato starch Patwardhan (J. Indian Inst. Sci. 1930, 13, A, 31) obtained four different dextrins.

Dextrin I has $[\alpha] + 174\ 0°$
„ II „ $+155\ 9°$
„ III „ $+170\ 6°$
„ IV „ $+184\ 2°$

Viswanath and Suryanarayana (J. Inst. Brew. 1925, 31, 425) found that both at low and high temperatures the hydrolysis of starch by cholam malt is slower than that by barley malt in the earlier stages, but eventually the rate for cholam malt overtakes that for barley malt. They concluded that two enzymes were concerned in the reaction an amylase converting starch into dextrin and a dextrinase further hydrolysing the dextrin to maltose

Acharya (Indian J Agric. Sci 1934, 4, 476) has studied the hydrolysis of starch by enzymes in the malt of cholam The optimum reaction and temperature of the active maltase are p_H 4 2 and 48° respectively, thus resembling that of maize and barley. A study of the liquefying and saccharifying properties of the diastases from cholam and barley malt indicates differences which are due to different contents of α- and β amylase.

Mineral Constituents —Ash analysis of four samples of Kaffir corn by Baird and Francis (*l.c.*) are summarised by Winton as follows :

	K_2O %	Na_2O_2 %	CaO %	MgO %	Fe_2O_3 %	P_2O_5 %
Minimum .	24 82	0·94	1 46	15 25	1 18	37 47
Maximum	29 78	2 42	2 15	18 86	2 08	46 72
Average . .	27 17	1 18	1 80	17 34	1 57	43 04

	SO_3 %	SiO_2 %	Cl %	C %	Sand %
Minimum .	0 17	0 96	0 44	0 17	2 88
Maximum .	1 22	4 15	0 58	0 31	5 73
Average .	0 52	2 16	0·49	0 25	4 00

Vitamins.—M. C. Smith (J. Agric. Res. 1930, 40, 1147) compares the vitamin A content of the grain sorghums hegari and yellow milo with yellow maize Yellow maize is 20 times as rich in vitamin A as hegari and 10 times as rich as yellow milo. Copeland and Fraps (Texas Agric. Exp Sta. Bull 1932, No 473) fed sorghum silage to dairy cows and found that it was not possible to give sufficient to provide the normal vitamin A requirements for maintainance, while the milk produced had a low and variable vitamin A content. Fomin (Arch Tierernährung u. Tierzucht, 1932, 8, 150) found that green sorghum contains a sufficiency of vitamin C, but to provide normal requirements of vitamin B it must constitute 20% of the ration. By the ensilage of sorghum the content of B and C is reduced, but vitamin D is unaffected. Reder (Proc.

Oklahoma Acad. Sci. 1934, **14**, 50) gives values for the content of vitamins B and B_2.

SORGHUM JUICE AND SYRUP.—Martin and others (J. Agric. Res. 1931, **42**, 57) examined the leaf and internode juices of seven varieties of sorghum and determined their freezing-point depression and conductivity. The total solids of the internode juices varied from 6·5 to 14·3%. Honey sorghum yields 15–238 (average 75) gallons of syrup per acre; 30–45% of the weight of the cane is obtained as juice. The sugar content varies from 5·7–14·7% (Ark. Agric. Exp. Sta. Bull. No. 241, 1929). The most important source of colour in sorghum syrup is lævulose. According to Willaman and Easter (Ind. Eng. Chem. 1929, **21**, 1138) the colour value as measured by the Pfund colour grader varies linearly with the logarithm of the concentration (in degrees Brix) and with the p_H.

The iron content of sorghum syrup is high (0·0147%) owing to the acidity of the original juices and evaporation in iron pans (Sheets and Sulzby, J. Home Econ. 1934, **26**, 431).

The jellying of sorghum syrup on evaporation and the difficulty in filtration are due to the presence of starch. Preliminary treatment of the juice with malt diastase greatly increases the rate of filtration and prevents the jellying of the finished product (Sherwood, Ind. Eng. Chem. 1923, **15**, 727, 780), Willaman and Davison (Ind. Eng. Chem. 1924, **16**, 609).

PHYSIOLOGICAL CHEMISTRY OF SORGHUM.—Acharya (Madras Agric. J. 1931, **19**, 157) has done some experiments on the growth and rate of adsorption of mineral nutrients. The tissues are richest in plant nutrients at the flowering stage or immediately following it. Taking an average crop of cholam to yield about 1,000 lb. of grain and 2,000 lb. of dry straw per acre, the mineral nutrients removed by the crop are, per acre:

Nitrogen	35 lb.
Phosphoric acid	10 lb.
Potash	32 lb.

Potash fertilisers increase the total sugars and sucrose in sorghum (Poromarenko, Nauk. Zapiski Tzuk. Prom. 1933, **10**, No. 27, 165).

Miller (J. Agric. Res. 1924, **27**, 785) measured the daily variation of carbohydrates in the leaves of sorghum and maize and found that the amount of dry matter per unit leaf area was always greater in the sorghum.

In connection with storage Coleman and others (U.S. Dept. Agric. Tech. Bull. 1928, No. 100) measured the respiration of grains and found that at high humidities damaged kernels respire more vigorously than do normal kernels.

Valuable crosses between sugar cane and sorghum have been developed; Viswanath and others (Indian J. Agric. Sci. 1934, **4**, 210) have experimented with these crosses and have recorded the analysis of the juices in relation to the maturity periods.

Antoniani (Atti R. Acad. Lincei, 1935, [VI], **21**, 192) records the enzymic transformation by the embryos of *Sorghum saccharatum* (sugar grass) of sodium phosphoglycerate into pyruvic acid, the yield of the latter being 25–27% of the theoretical.

V. Cuculescu (Z. Unters. Lebensm. 1934, **68**, 651) gives the analysis of the seeds, stems, and syrup of sugar grass.

MANUFACTURE OF BLEACHED PULP FROM SORGHUM STALKS.—Yamamoto (Rept. Lab. Sci. Manchuria Rly. 1929, 26; J. Cellulose Inst. Tokyo, 1928, **4**, 53) digested the stalks first with water at 100°–120° for ½–1 hour, and then with 12% of caustic soda at 130°–140° for 3–4 hours. A 46% yield of light brown pulp was obtained which bleached with 2·97% of available chlorine, giving a 36% yield of bleached pulp. It is estimated that the annual production of stalk is about 14·4 million tons.

Common Millet.—*Panicum miliaceum* L.

Composition of common millet and products, Bersch (Landw. Versuchs-Stat. 1895, **46**, 103):

	Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Ash. %
Rough millet .	9·40	11·56	3·29	62·97	10·00	2·88
Bran . . .	10·27	6·68	2·33	19·50	52·50	8·72
Bran . . .	9·65	6·25	2·38	28·58	43·78	9·36
Polish . . .	8·83	18·06	18·48	35·02	11·07	8·44
Polish . . .	9·00	18·37	16·50	42·61	6·38	7·14
Decorticated millet[1] . .	9·77	13·06	2·84	72·99	0·46	0·88
Decorticated millet[1] . .	9·16	11·40	2·81	75·14	0·23	1·26

[1] Extreme sizes.

Chamberlain (*l.c.*) gives the analysis of 38 samples of Proso. The range and average composition are:

	Water. %	Protein ($N \times$ 6·25). %	Fat. %	N-free extract. %	Fibre. %	Ash. %
Minimum . .	8·15	10·0	2·88	65·69	4·58	2·78
Maximum .	10·93	17·94	3·78	75·22	10·89	5·65
Average . .	8·93	12·77	3·27	71·23	8·95	3·78

PROTEINS (Winton *op. cit.*, p. 125).—In samples analysed by Bersch (*l.c.*) the protein nitrogen and amide nitrogen in millet and its products were as follows:

	Protein N	Amide N
Rough millet .	1·83	0·02
Bran . . .	0·96–1·04	0·03–0·04
Polish . . .	2·71–2·79	0·09–0·23
Decorticated .	1·76–1·94	0·01–0·33

The nuclein ranged from 0·70 in the polish to 0·40 in the decorticated millet.

CARBOHYDRATES (Bersch, *l.c.*).—

	Starch.	Sugar, etc.
Rough millet .	62·56	0·31
Bran . . .	19·03–27·83	0·47–0·75
Polish . . .	34·12–41·59	0·90–1·02
Decorticated .	72·56–74·40	0·37–0·74

MINERAL CONSTITUENTS.—The composition of the ash of millet, given by Haskins (Mass. Agric. Exp. Sta. 1919, Spec. Bull) in terms of parts per thousand of the grain, as recalculated by Winton in percentages of the ash:

K_2O	Na_2O	CaO	MgO	P_2O_5	SO_3	Cl	Undetermined.[1]
11·2	1·4	0·7	9·5	22·0	0·3	0·3	54·6

[1] Mostly silica.

Konig reports similar figures including silica 56% (Chem. Mensch. Nahr-Genussm. Berlin, 1920, 2, 873).

Pearl Millet.—*Pennisetum americanum* Schum = *P. tyhoideum* Rich. = *Penicillaria spicata* Willd. Extensively grown in Africa, India, and other Asiatic countries. In sub-tropical Europe and America it is grown as fodder. In Africa it is known as duchn or dohan.

Chemical Composition.—As analysed by Church (Watts' Dict. Econ. Prod. India, Calcutta, 1889, 6, Part 1, 30), and Balland (Comp. rend. 1902, 135, 1079).

	Water %	Protein %	Fat %	N free extract %	Fibre %	Ash %
Church .	11 3	10 4	3 3	71 5	1 5	2 0
Balland—						
Minimum	11 0	8 78	2 35	66 07	1 35	0 80
Maximum	14 0	16 10	6 25	71 17	3 85	2 10

Italian Millet (*Setaria italica*).—Kondo (Imp. Jap. Inst. Nutrition, Bull. Soc hyg. aliment, 1927, 15, 481, 524) records the following analysis:

	%
Water . . .	. 13 57
Crude protein	11 12
Albuminoids .	10 36
Fat	5 32
N-free extract	. 63 68
Fibre . .	. 1 71
Ash .	. 0 87

Protein (Kondo).

N distribution as percentage of total	%
Humin	. 2 54
Amide	12 03
Arginine	. 0 71
Cystine	. 2·21
Histidine	11 81
Lysine	. 6 05
Mono amino	49 43
Non-amino	4 76

Vitamins —Millets show considerable variations in their content of fat soluble vitamin, and even in specimens which are richest in this factor the content appears to be insufficient to promote the growth of rats for long periods (Steenbock and others, J. Biol Chem. 1923, 56, 345).

According to Corkill (Lancet, 1934, 226, 1387) the fundamental condition causing pellagra in the Sudanese millet eaters is a lack of cholesterol and vitamins A and D in the food, lack of C being a contributory factor Vitamin D and not water soluble B_2 is the antidermatitis vitamin.

Physiological Chemistry —Schleusener (Z. Pflanz. Düng. 1926, A, 7, 137) showed that the course of adsorption of plant nutrients by different varieties of millet during the growing period is similar to that of the summer cereals, particularly barley.

Production of dry matter lags behind the intake of plant nutrients, which is largely completed by the time of flowering. During the first three fortnightly periods of the growing season the course of adsorption is not markedly influenced by the manuring. Only in the case of nitrogen was the course of adsorption affected by manuring, and the greater the amount of nitrogen given the more did adsorption provide formation of dry matter. The plant nutrient requirements of millet appear to be less than those of barley.

Borodina (Bull. Appl Bot. Leningrad, 1931, 27, No. 5, 171) records experiments on the influence of nutrition on the time of appearance of the ears of millets. This is not affected by N or K but lack of P causes delay. Schaffer-Kircher (Arch. Pflanzenbau, 1933, 10, 324) has investigated the influence of soil reaction on the germination of millet and maize. In general millet prefers the more acid conditions and the p_H range of germination is wider than that of maize.

A fermented beverage called "Bosa" is made from millet. Heiduschka and Dantscheff (Pharm. Zentr. 1931, 72, 337) give the following directions A very thick mash of finely ground millet is boiled and cooled several times and inoculated with an infusion of ground chick-pea and air-dried embryos of millet After keeping overnight at room temperature, the diluted mash is filtered through wire gauze and allowed to ferment further. The resulting yellowish-brown beverage in which are suspended the finest particles of the millet is termed "Bosa" and contains at the end of 13 days 0 515% of ethyl alcohol, 0 493% of lactic acid, and 0 0975% of acetic acid.

Eleusine coracana Gaertin.

This cereal, also known as African millet, like the sorghums and pearl millet (*Pennisetum typhoideum* Rich.) is extensively grown in Central and Southern Africa and to some extent in Egypt and Abyssinia. Under the name "ragi" it is the staple cereal crop of the state of Mysore, India (Narayana and Norris, *l c.*).

Composition of Coracan (Winton, *op cit.* p. 178).

	Water %	Protein %	Fat %	N free extract. %	Fibre %	Ash. %
Church—						
Whole grain	12 5	5 9	0 8	74 6	3 6	2 6
Husked grain	13 2	7 3	1 5	73 2	2 5	2 3
Adolph . .	8 50	5 84	5 75	74 26	2 01	3 64
Narayana and Norris, I .	0 00	6 90	1 82	85 23	3 27	2 78
Narayana and Norris, II .	0 00	9 83	1 61	82 50	3 54	2 52

Proteins —Narayana and Norris (*l c.*) found that the protein matter of the grain consisted largely of a prolamine to which they gave the name *eleusinin*.

The finely ground grain was extracted with three times its weight of 70% alcohol. The extract was filtered and the clear yellow liquid was evaporated under reduced pressure until the first signs of precipitation. The liquid was then filtered and poured with constant stirring into ten times its volume of distilled water. A milky fluid was produced from which the protein was precipitated by the addition of sodium chloride. The precipitate was purified by solution in 70% alcohol and reprecipitated. After washing with water the precipitate was dried and extracted

with ether to remove the fat. The final product contained 15·9% N and both tyrosine and tryptophan. There was no P present and cystine was probably absent.

The ultimate composition was :

	%
C	53·29
H	7·35
N	15·91
O	23·34

The nitrogen distribution was determined in a mixed sample by the Van Slyke method (J. Biol. Chem. 1911, **10**, 15) as modified by Plimmer (J. Biol. Chem. 1925, **10**, 1004). Expressed as percentages of total nitrogen :

Humin.	
Insoluble	0·87
Soluble	0·28
Amide	20·52
Basic.	
Arginine	2·60
Histidine	2·69
Lysine	0·64
Non-basic.	
Amino	69·03
Non-amino	2·13

ENZYMES.—Patwardhan and Narayana (J. Indian Inst. Sci. 1931, **13**, A, 38) found that the amylase of "ragi" had greater saccharifying power than cholam malt and maize malt enzymes, but less than that of barley malt amylase. The optimum temperature lay between 55° and 60°. The optimum reaction was between p_H 4·86 and 5·07. W. R. S. L.

OATS.

Cultivated oats include eight common species of the genus *Avena*. Their cultivation is practically confined to Europe and North America, and occupies about half as great an area as wheat. Owing to their hardness, they were very little used for human food before the introduction of machinery, and 95% of the crop is still consumed by animals and poultry.

Oats vary in composition as wheat does. A typical analysis of crushed oats (Milling, 1933, **80**, 340) gave :

Moisture %	Oil. %	Albuminoids. %	Digestible carbohydrates. %	Woody fibre. %	Mineral matter. %	Silica. %
13·45	6·77	11·12	56·92	9·14	2·60	0·85

Other analyses have been carried out by Aitken (Trans. H. and Ag. Soc. 1901, v, **13**, 292, 293), Wilson (*ibid.* 1903, v, **15**, 183) and Atwater (U.S. Dept. Agric. Exp. Sta. Bull. 1899, No. 28) and a complete elementary analysis by Bertrand and Ghitescu (Compt. rend. 1934, **199**, 1269). The variations due to the variety of oat are the most important, especially for the manufacture of oatmeal, and the proportion of husk to kernel is the most significant factor. Oats are remarkable for their high fat content and are also rich in protein, constituting a valuable and concentrated foodstuff. They are, however, deficient in vitamin A, traces of which are found in the oil only (Meyer and Hetler, J. Agric. Res. 1931, **42**, 501). Oat straw is valuable as fodder, since it is cut while the transference of food to the ripening grain is still incomplete (Milling, 1933, **80**, 340).

In addition to human and animal foods, an important product is furfural, first made from oat hulls by the Quaker Oat Co. about 1924, This process was for long the only commercial source of furfural, and is still the largest source.

E. A. F.

RICE.

Contents.—Introduction; Yields; Milling of Rice; Composition of Rice and Rice Products Proteins; Fat; Carbohydrates and Enzymes; Mineral Constituents; Minor Elements; Rice Husks; Rice Straw; Storage; Vitamins; Organic Phosphorus Compounds; Rice Products as Feeding Stuffs; Physiological Chemistry; Analytical; Wild Rice.

RICE (*Oryza sativa*, L.).—A swamp grass which has been cultivated in Asia from remote ages. It was known in China and Japan before 3000 B.C. It is the staple cereal of the East, being extensively grown in China, Japan, India, Ceylon, Burma, the Malay Archipelago, and Siam. In the New World it is grown in the West Indies, Central America, and Southern States of U.S.A. In Europe it is cultivated in Italy and Spain.

Rice in its original state, *i.e.* unhusked, is sometimes known as padi or paddy.

There are upwards of 2,000 named varieties, but these may be classified into two distinct groups: glutinous rice and non-glutinous rice. The glutinous rice, sometimes assigned the specific name of "glutinosa," with coarse, large, red, purple, or blackish grains, forms the staple food of the people in the north of Siam.

Some of the other varieties of rice have been wrongly described as distinct species, *e.g.* hill padi or mountain rice, *O. montana*; quick-growing rice, *O. praecox*. Quick-growing rice may take only 70 days to mature, whilst some of the slower growing varieties will occupy the land for 9 months.

Rice may be sown broadcast or by transplanting from nurseries.

In Malaya a double transplanting is favoured. Rice is the only important crop that is grown in water. In Siam, Indo-China, and Bengal there is a variety of broadcasted padi known as floating rice, grown in certain areas where at the end of the wet season the water on the fields rises to a great height. The rice planted in these fields is able to keep pace with the rising water. The growing tips of the plant always remain above the surface and from the submerged roots of the stems subsidiary rootlets are sent off into the muddy water. Harvesting is done from boats followed by a final gleaning after the floods have subsided. The stems of floating padi sometimes reach the amazing length of 6

metres (Ladell, Trop. Agric. 1931, LXXVII, 173.

Principal Rice-growing Countries — Yield and Area under Cultivation.

(From "International Yearbook of Agricultural Statistics," 1934–1935.)

	Area in Hectares	Quintals per Hectare	lb per acre
Europe.			
Spain	46,103	63 7	5,683
Italy	130,722	47 2	4,211
America			
U S A	316,100	24 7	2,204
Br Guiana	28,712	19 5	1,740
Asia.			
Ceylon.	340,000	9 7	865
China	18,398,800	21 3	1,900
Manchuria	203,850	16 6	1,481
Formosa	666,966	25 3	2,257
Br. India	32,789,600	13 9	1,240
Br Malaya	297,331	17 5	1,561
Burma	5,125,700	13 5	1,205
Indo-China	5,332,000	9 9	883
Japan . .	3,146,666	30 6	2,730
Philippines	2,004,030	11 6	1,035
Siam	2,932,830	15 7	1,401
Java	3,398,200	15 7	1,401

The highest recorded yield in Siam without the use of fertilisers is 3,562 lb. per acre (Ladell, *l c*)

The Milling of Paddy.—The first process is the removal of husks or hulls, leaving what is called "brown rice" The brown rice then passes through conical mills or pearling cones which remove the outer skin and produce skinned rice, sometimes called Loonzein or white rice In the next process the white rice is polished by whirling the grain in contact with felt or leather pads. Finally the rice is glazed Various mineral materials, such as talc, steatite, mica, kaolin, or gypsum are used, with or with out the addition of glucose, glycerine, or mineral oil. Glazing is not often practised in the East.

Strictly speaking, "rice meal" is the bran resulting from skinning the rice in the conical mills or pearling cones, but the term is some times applied to the polishings or to a mixture of the bran and polishings. "Cargo rice" is the mixture of husked rice and paddy from the hullers. "Broken rice" is composed of the broken grains separated by sifting the product from the different processes, and varies in composition according to whether it comes from the hulls, conical mills, or polishers According to Fraps (*vide infra*) the American process is briefly as follows:

1 "Stones" remove the husk or hulls from the purified paddy.

2 "Stone bran reel" which separates the "chits" consisting of broken rice and rice hulls, and "stone bran," consisting of a mixture of broken rice and rice hulls.

3 The paddy machine separates the mixture of brown rice and paddy rice. The brown rice goes to the "hullers"

4. "Hulling ' This term is one that has led to much misunderstanding, as it is the bran that is removed, not the hulls The huller bran is usually mixed with the "stone bran" and the mixture is known as "rice bran"

5. "Pearling cones" erode much of the outer covering of the rice grain, resulting in the production of "cone meal"

6. "Brushes," consisting of cylindrical frames covered with hide or skin, revolving rapidly inside a cylindrical cover of a close mesh wire screen This process rubs off the remainder of the thin outer skin of the rice grain and gives rise to the "polishings."

Fraps (Texas Agric Exp Sta 1911, Bull 191) made a comprehensive investigation of rice milling products and by products (*see* Winton, "Structure and Composition of Foods," Vol 1, p. 140, Chapman and Hall, Ltd, London, 1932)

Composition of Rice and its By Products. (Fraps).

	No of samples	Water %	Protein %	Fat %	N free extract %	Fibre %	Ash %	Sand %
Products								
Rough rice	9							
Min.		9 64	7 23	1 39	60 95	6 99	4 30	4 24
Max. . .		13 50	8 95	2 07	66 41	10 10	6 42	4 24
Aver. . .		11 68	8 09	1 80	64 52	8 89	5 02	4·21
Brown rice.	16							
Min. . . .		10 55	7 90	1·41	71 39	0 78	0 95	0 05
Max. . . .		14 41	10 65	2 56	76 74	1·51	1·54	0 28
Aver. . . .		12 16	9 13	2 00	74 53	1 08	1·10	0 10
Head (fancy) rice:	8							
Min. . . .		11 91	6 60	0 25	75·11	0 35	0 30	0 06
Max. . . .		13 84	10 04	0 98	79 85	0 48	0 94	0 13
Aver. . . .		12 57	9 01	0 50	77 02	0 40	0 50	0 09

Composition of Rice and its By-Products (Fraps).—*continued.*

	No. of samples.	Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Ash. %	Sand. %
By-products.								
Stone bran :	22							
Min. . . .		6·79	7·46	4·28	29·63	14·09	9·74	6·63
Max. . . .		11·64	11·78	11·55	47·97	25·94	20·99	17·97
Aver. . . .		9·69	9·77	7·66	36·73	20·92	15·23	12·06
Cone bran :	28							
Min. . . .		8·54	12·50	11·78	38·35	2·50	5·39	0·39
Max. . .		11·50	16·52	20·32	55·94	8·79	8·61	1·77
Aver. . . .		9·77	15·39	15·97	46·13	5·66	7·08	0·88
Rice polish :	10							
Min. . . .		8·46	11·13	5·62	59·43	1·52	2·41	—
Max. . . .		10·76	14·45	12·95	67·28	2·79	5·57	—
Aver. . . .		9·91	12·88	9·07	61·81	2·12	4·21	—
Rice hulls :	11							
Min. . . .		6·11	1·78	0·54	24·56	31·43	14·83	13·69
Max. . . .		10·95	5·00	1·98	38·83	46·37	22·00	20·84
Aver. . . .		8·49	3·56	0·93	29·38	39·05	18·59	17·52

Warth and Darabsett (Dept. of Agric. Burma, 1913, Bull. No. 10) record the chemical composition of paddy mill products. Brown rice will produce: polished rice 55%, broken rice (all grades) 30%, dust 4%, and meal 11%. They give the composition of the ash as follows:

Mineral Constituents

No. 1.

	Paddy. %	Skinned rice (Loonzein). %	Polished rice. %
Silica	4·28	0·16	0·03
Iron and aluminium phosphate . . .	—	0·10	0·01
Lime	—	0·03	0·02
Magnesia	—	0·20	0·05
Phosphoric acid . .	0·54	0·67	0·23
Potash	—	—	—
Nitrogen	0·91	1·11	0·99

No. 2.

	Paddy. %	Skinned rice. (Loonzein). %	Polished rice. %
Silica	3·08	0·10	0·01
Iron and aluminium phosphate . . .	—	—	—
Lime	—	0·02	0·01
Magnesia	—	0·19	0·05
Phosphoric acid . .	0·57	0·69	0·24
Potash	—	0·30	0·08
Nitrogen	0·91	1·09	0·98

Mineral Constituents of By-Products

	Meal from polishers. %	Meal from cones. %	Mill dust. %	Husk. %
Silica (SiO_2) . .	0·970	1·402	11·500	17·18
Lime (CaO) . .	0·040	0·061	0·068	—
Magnesia (MgO) .	0·175	0·990	0·449	—
Phosphoric acid (P_2O_5)	2·816	3·858	1·092	0·041
Potash (K_2O) . .	—	1·464	—	—
Nitrogen (N) . .	1·640	1·880	1·127	0·027

The outstanding figures are the high proportion of silica in the husk and in the mill dust, which consists largely of broken husk. The meals contain large amounts of phosphoric acid, potash, and nitrogen.

Parboiling (Charlton, Agric. Res. Inst. Pusa, 1923, Bull. No. 146).—The village method of parboiling paddy is to place it in a receptacle, copper pots, earthenware pots, or kerosene oil tins. The paddy is covered with water to a level of almost 2 ins. above the grains. The receptacle is heated until the contents boil and the glumes commence to split open. The paddy is then spread on mats to dry. This takes from one to two days. The paddy is ready to pound when the grains have become hard. Parboiled rice is more sustaining than white rice. When cooked it remains sweet for a longer period than white rice and has a pleasanter taste. Millers have adopted the village method to large scale operations. Parboiling reduces breakage and milling losses. Thus the process increases the milling output and profits to the miller.

Parboiled rice is more nutritious than raw rice. This is due partly to the fact that during the process of parboiling, vitamin B_1 penetrates into the endosperm layer and is not entirely lost in polishing. Moreover, parboiled rice is generally richer in both nitrogen and phosphorus than raw rice, even when polished to the same degree, but as a rule the parboiled rice is never polished so severely as raw rice, which is another factor in favour of a higher nutritive value (Sreenivasan and Das Gupta, Current Sci. 1936, V, 75).

Jones and Taylor (U.S. Dept. Agric. Circ. No. 340, 1935) found that increases in "head rice" (best polished rice) due to parboiling were independent of the period of soaking, temperature, or amount of steaming. These factors, however, did affect the colour and texture of the product.

Joachim and Kandiah (Trop. Agric. 1928, LXX, 195) have analysed Ceylon paddies, rices, and milling products.

The hill paddy is richer in organic constituents, but poorer in minerals, chiefly phosphoric acid, than the irrigated paddies (*see* Cochran's "Ceylon Manual of Chemical Analyses," 1895). The pure line paddies appear to be richer in proteins, fats, and minerals than the ordinary cultivated variety. The average chemical composition of the Ceylon paddies is similar to that of Indian paddies (Sen, Agric. Res. Inst. Pusa, 1917, Bull. No. 70).

Le Clerc (Cereal Chem. 1932, 9, 600) gives the following figures for Japanese rice:

	Unpolished (brown rice)	Polished	Glutinous rice
Weight of 100 kernels	2 011	1 824	2 650

COMPOSITION OF DRY MATTER

	Unpolished %	Polished %	Glutinous %
Protein	8 67	8 15	8 63
Fat	2 45	0 37	2 89
Fibre	0 88	0 16	1·12
Carbohydrates	86 70	90 79	86 00
Ash	1 22	0 36	1 36

Takahashi and Sato (J. Coll. Agric. Tokyo, 1913, 5, No. 2, 135) analysed 44 samples of polished rice specially prepared and "whitened" for brewing saké.

	%
Moisture	12–15
Sugar	0 51–0 79
Fat	0 24–1·18
Total Nitrogen	1·3–1·4
Non protein nitrogen	0 11–0 36
Ash	0 29–0 38

The pounding and polishing of rices result in a marked decrease in their fat, phosphoric acid, fibre and, to a lesser extent, protein contents. Thus the "silver skin" or "aleurone" layer of the rice grain contains the more valuable nutritive constituents. Parboiling affects unappreciably the chemical composition of rices, except for a slight falling off of the fat content. Bran is very rich in fat, protein, and phosphoric acid.

The composition of rices from different countries is given by Wiley (U.S. Dept. Agric. Bur. Chem. 1898, Bull. 13, 1182). Wiley tabulates the maxima and minima, and means of the various constituents. The following figures represent typical samples:

	Wt in grams of 100 grains	Water %	Protein %	Fat %	Sol carbohydrates %	Crude fibre %	Ash %
Unhulled	3 00	10 5	7 5	1 6	67·4	9 0	4 0
Hulled	2 50	12 0	8 0	2 0	76 0	1 0	1 0
Hulled and polished	2 20	12·4	7 5	0 4	78 8	0 4	0 5

Borasio (Giorn risicolt, 1929, 19, 131; 1930, 20, 71, 88) reports the analyses of polished rice, rough rice, and gemma (germ):

COMPOSITION OF RICE GERM.

Gemma (germ)	Water. %	Protein. %	Fat. %	N free extract %	Fibre %	Ash. %	Sand %
Min.	10 50	10 50	10 70	52 50	3 30	7 40	3 70
Max.	12 30	11 80	13 40	55 80	3 90	8 00	4 10

RICE PROTEINS.—Tadokoro *et al.* (J. Coll. Agric. Sapporo, 1927, 19, 93) compare the physico chemical properties of the rice proteins separated into four fractions, soluble in water, NaCl sol., NaOH sol., and alcohol respectively.

Glutelins.—Rosenheim and Kajiura (J. Physiol. 1908, 36, No. 6), investigating rice proteins, found a glutelin which they named oryzenin, small amounts of albumin and globulin were reported but not prolamine (gliadin).

Larmour (J. Agric. Res 1927, 35, 1091) describes the preparation of alkali soluble proteins (glutelins) from rice and other cereals and tabulates their N distribution by Van Slyke's method.

Jones and Csonka (J. Biol. Chem. 1927, 74, 427) prepared the glutelin by extracting the rice with 0 2% NaOH and treating the extract with $(NH_4)_2SO_4$ to 3% saturation. The product so obtained has an iso-electric point of p_H 6 45 and a higher content of nitrogen, with a different N distribution compared with the preparations of other workers.

Jones and Gersdorff (J. Biol. Chem. 1927, 74, 415) obtained 2 4% of a glutelin from polished rice but none from rice bran. In contrast with wheat endosperm, which contains two different glutelins, rice endosperm contains only one.

Kondo and Hayashi (Mem. Coll. Agric. Kyoto Imp. Univ. 1926, No 2, 37, 55) used 0 05*N*-NaOH to dissolve the glutelin and 0 05*N* acetic acid to flocculate it, maximum flocculation occurring near absolute neutrality. They record the N-distribution for the anhydrous protein so prepared. Kondo *et al.* (*ibid* 71) studied the influence of sodium acetate, sodium chloride, potassium chloride, and lithium chloride on solutions of rice glutelin. These salts carry the optimum part of flocculation to the acidic side, and the apparent iso-electric reaction of the protein is variable according to the salt used and its concentration (Kondo and Hayashi, *ibid*. 83). In contradistinction to the theory propounded by Robertson and by Wington, the authors conclude, from their results, that refractive indices of solutions of sodium rice glutelinate or sodium caseinate are not linearly related to their concentrations. The authors, moreover, maintain that the determination of the nitrogen-equivalent refractivity of

the protein indicates the degree of dissociation of the protein salt, and conclude that to an ampholyte such as protein belong different nitrogen-equivalent-refractivities, according as the protein behaves as a kation or an anion.

Tadokoro (J. Coll. Agric. Sapporo, 1925, **14**, 129) concluded that glutinous rice contains more oryzenin than common rice. The oryzenin (*a*) *prepared from common rice differs from that* (*b*) prepared from glutinous rice, in iso-electric point, nitrogen, sulphur, and phosphorus content and in its physical constants. On the determination of the amino-acids it was observed that in (*a*) there was a predominance of ammoniacal, arginine and lysine nitrogen, while in (*b*) there was an excess of monoamino, histidine and cystine nitrogen. The content of tyrosine and tryptophane is the same in both forms.

Tadokoro *et al.* (J. Coll. Agric. Sapporo, 1926, **16**, 73) divided 16 samples of common Japanese rices into two groups: (*a*) those employed for fermentation to saké and (*b*) those not so employed. The oryzenin prepared from these differed in physico-chemical properties. The ash content of (*a*) is always 79–95% of (*b*), sulphur and phosphorus of (*b*) are more than (*a*). The sp. rot. power of (*a*) is considerably lower than (*b*). The iso-electric point of (*a*) is more acidic than that of (*b*). The silver salts and the N-distribution are different. Takahashi *et al.* (J. Coll. Agric. Tokyo, 1913, **5**, 134) separated proteins from rice prepared for brewing purposes using Osborne's method (Amer. J. Physiol. 1908, **20**, No. 1 and No. 4). Four kinds of protein were obtained: albumin, soluble in water; globulin, soluble in 10% NaCl; prolamine, soluble in 80% alcohol; and glutelin (Rosenheim's oryzenin), soluble in dilute alkali.

The three kinds of proteins, albumin, globulin, and oryzenin, are utilised by saké yeast and *Aspergillus Oryzae*; prolamine is not.

DISTRIBUTION OF NITROGEN IN RICE GLUTELIN BY VAN SLYKE'S METHOD.

Grams per 100 *g. of Protein.*

	Jones and Csonka.	Osborne *et al.*[1]	Kondo and Hayashi.[2]
Arginine	11·13	9·15	8·40
Histidine	2·39	3·32	3·65
Lysine	4·73	4·26	6·48
Cystine	2·35	1·26	8·95

[1] J. Biol. Chem. 1915, 22, 259.
[2] Mem. Coll. Agric. Kyoto, 1926, 2, 37.

Prolamines (gliadins) are present only in small quantities in the inner endosperm of rice. Suzuki, etc. (J. Chem. Soc. Tokyo, 1908, **29**, 3) found only 0·11% of nitrogen soluble in 60% alcohol, but 1·16% in bran.

Hoffman (J. Biol. Chem. 1925, **66**, 501), by extraction with hot 70% alcohol obtained from polished rice 0·12% of a protein; C 55·92, H 6·49, N 16·22, and S 1·14%.

Globulins and Albumins.—Rosenheim and Kajiura (*l.c.*) found 0·14% of a globulin. Suzuki, etc. (*l.c.*) found in white rice 0·17% N soluble in 10% salt solution and 1·37% in bran. By extraction of rice endosperm with salt solution (5%), Jones and Gersdorff (J. Biol. Chem. 1927, **74**, 415) obtained 0·09% of a globulin coagulating at 74° and 0·07% of a second globulin coagulating at 90°. Rice bran gave 2·88% of globulin and 0·13% of albumin. Kondo and Ito (Mem. Coll. Agric. Kyoto Imp. Univ. 1931, No. 11, 31) demonstrated the presence of two globulins in polished rice, *one crystallisable from saline solution and the* other non-crystalline. They found that the latter contained more cystine, histidine, and arginine than the former. Jones, in collaboration with Gersdorff and Csonka (*l.c.* 422), recorded the following composition of the two globulins.

	Globulin coagulable at 74° C. %	Globulin coagulable at 90° C. %
Cystine	2·25	2·89
Arginine	7·85	15·18
Histidine	2·42	3·01
Lysine	7·14	3·63
Tryptophane	2·69	2·32
Tyrosine	5·60	7·53

Amino-Acids of Rice Proteins.—Jodidi (J. Agric. Res. 1927, **34**, 309) found that the total nitrogen in oven-dried rice varied from 1·7–1·24%. Polypeptides and free amino-acids occur in brown rice, amino-nitrogen amounts to 0·75–1·02% of the total N. Corresponding figures for acid amide N are 0·14–0·23%, and for polypeptide N, 0·85–1·15% (Miki, Arb. mid. Univ. Okayama, 1933, **3**, 499). The protein from rice embryo yielded on hydrolysis arginine and traces of *histidine*, but no lysine.

According to Suzuki, *et al.* (J. Coll. Agric. Tokyo, 1909, **1**, 77), the dry matter of brown rice contained 1·2% N of which 1·165% existed as true proteins. The glutelin obtained by Ritthausen's method yielded on hydrolysis: alanine 3·7, leucine 14·3, aspartic acid 0·4, glutamic acid 14·5, tyrosine 0·5, proline 3·3 phenylalanine 2·0, lysine 0·86, histidine 0·81 arginine 1·6, and ammonia 2·33%.

Marañon and Cosme (Philippine J. Sci. 1935, **57**, 289) recorded the nitrogen distribution in bran containing N = 14·15% protein. Non-basic N accounts for 70·9%, and basic N for 16·4% of the total.

OIL OF RICE.—The oil of rice is concentrated chiefly in the bran from the conical mill and in the polish from the polishers.

Winton (*op. cit.* I, 147) tabulates the constants of rice oil obtained by various workers (*see* table on next page).

Phytosterol.—Tsujimoto (*l.c.*) obtained a phytosterol melting at 136°–137°C. from the unsaponifiable matter. Weinhagen (*l.c.*) obtained a saturated hydrocarbon, $C_{27}H_{48}$, m.p. 80°, from the phytosterol by fractional crystallisation from alcohol.

Nabenhauer and Anderson (J. Amer. Chem. Soc. 1926, 48, 2972) obtained 10% of oil consisting largely of free fatty acids. The unsaponifiable matter (5%) containing a phytosterol, myricyl alcohol, dihydrositosterol, and

RICE OIL.

	Sp. gr. 15·5° C.	Ref. Index 20° C.	M.p. °C.	Saponification no.	Iodine no.	Reichert-Meissl no.	Hehner no.	Acid no.	Unsap. matter
Browne	0·8907	—	24	193·5	91·6	1·1	*	166·2	—
Tsujimoto . .	0·9273	1·4742	—	184·9	107·6	—	†	34·7	4·8
Garelli:									
Extracted .	—	—	25–26	186·0	99·7	—	95·2	90·0	3·2
Expressed . .	0·918	—	—	179·4	—	—	94·3	13·8	0·7
Expressed	0·913	—	—	189·7	—	—	95·0	101·5	0·9
Takahashi									
North Japan	0·9236	1·4704	—	189·9	105·8	0·6	96·6	122·2	3·7
South Japan	0·9254	—	—	183·8	104·7	0·7	96·0	14·4	4·0
Korea .	0·9276	1·4713	—	183·5	108·6	1·2	92·1	11·9	4·2
Formosa	0·9208	—	−5	192·2	103·1	1·7	94·1	81·3	3·9
Jamieson									
Rice Bran Oil . .	—	—	—	185·3	99·9	—	—	73·7	4·6
De Conno and Finelli .	—	—	24–25	189·1	100·8	—	95·1	101·2	1·4

* Mean molecular weight of insoluble acids 289·3; melting point 36°.
† Mean molecular weight of insoluble acids 259·4; melting point 38·5°, saponification number 216·3.

stigmasterol. No substance resembling Weinhagen's saturated hydrocarbon was identified. According to Antoniani (Atti R. Accad. Lincei, 1932, [vi], 16, 510) the phytosterols of Nabenhauer and Anderson (*l.c.*) *are mixtures of a* sterol, $C_{27}H_{46}O$ (m.p. 143°), with its dihydro derivative.

Tanaka (J. Biochem. Japan, 1933, 17, 483) examined the sterols of the rice embryo which on fractionation yielded myricyl alcohol ($C_{30}H_{62}O$) m.p. 86°–87°, and dihydrositosterol. Tanaka (*ibid.* 18, 1) also obtained evidence of the presence of ergosterol. Kimm and Noguchi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 1) obtained phytosterolin from the *ether extract of rice embryo. The solid acids* were myristic, behenic, palmitic, and cerotic acids. The bromination of the unsaturated acids yielded linoleic acid tetrabromide. The unsaponifiable matter contained 0.5% of ergosterol, also melissyl alcohol and dihydrositosterol.

WAX IN RICE.—Tange (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 275) obtained 0.03% of wax from rice polishings by extraction with boiling alcohol. After washing with ether *to remove fat, the wax was dissolved in benzene* and reprecipitated by the addition of methyl alcohol. The wax had a m.p. of 81.5°–82.5° and was identified by saponification as melissyl cerotate.

CARBOHYDRATES AND ENZYMES.—Frap's (*l.c.*) investigations showed that most of the disaccharides were concentrated in the bran, leaving very little in the milled rice.

	Reducing sugar, %	Disaccharides %	Pentosans %
Brown rice .	0·12	0·79	2·12
Fancy head rice .	0·14	0·17	1·75
Stone bran . .	0·78	1·15	13·87
Cone bran or meal	1·53	2·15	5·81
Polish . . .	1·27	2·26	3·47
Hulls or husks .	0·24	0·43	18·14

Marañon and Cosme (*l.c.*) record the carbohydrate distribution in bran containing 44.5% carbohydrate. 46.76% carbohydrate occurs as starch, 0.87% as reducing sugars, and 11.66% *as non-reducing sugars.*

Starch.—In common rice amylopectin is more abundant than amylose, while in glutinous rice the reverse is the case (Tadokoro, J. Coll. Agric. Sapporo, 1923, 13, 1; 1926, 16, 91), *cf.* Tanaka, Ind. Eng. Chem. 1912, 4, 578).

Warth (Mem. Dept. Agric. India, Chem. Series, 1914, III, 135), doing experiments on the fractional liquefaction of rice starch at various temperatures, found that the starch from glutinous rice liquefies at a lower temperature *than the starch of the non-glutinous rices.*

Komuro did some experiments on the saccharification of flaked rice with acids (J. Soc. Chem. Ind. Japan, 1931, 34, 166), the hydrolysis is slower than that of potato starch due partly to the different properties of the starch granule and partly to the presence of the amphoteric protein oryzenin which is deposited from the hot filtrate of hydrolysed rice on standing. Tao (Bull. Chem. Soc. Japan, 1930, 5, 209) showed that the chemical change undergone by *rice during cooking is mainly hydrolysis to* water-soluble reducing sugars and polysaccharides. These chemical changes resemble those taking place on the germination of rice seeds, except that the velocity of conversion of starch into soluble sugars is greater in the former, and the change of starch into CO_2 and H_2O takes place only in the latter. Sahasrabuddhe and Kibe (Indian J. Agric. Sci. 1935, V, 12) made a biochemical study of the starches from old and new grains of different varieties of rice to ascertain whether the rice starch undergoes any disintegration during storage. There was a difference of two years between the old and the new. As rices grow old they become more susceptible *to the action of hydrolysis.* Thus old rices are easier to digest than new rices. These differences are attributed to the presence

of an amylo-hydrolytic enzyme in the resting grain, which remains active and attacks the starch.

Sakurada, etc. (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 361), studied with the aid of X-ray and enzymic observations the change of β-starch $\rightarrow$ α-starch under varying conditions of temperature, dilution, and time. Matsumoto and Kise (Bull. Res. Inst. Fermentation, 1929, No. 102, 63) found that when rice malt is saccharified at 55° the buffer action of the solution first increases and then decreases, apparently due to the presence of lactic acid bacteria, but the p_H remains constant. The titratable acidity normally increases during saccharification. When soluble starch or rice paste is saccharified by diastase or malt extract the buffer capacity remains constant.

Jaschke (U.S.P. 1681118) describes a method for the extraction of starch from rice. The dry rice is ground to a degree of fineness sufficient to liberate the starch granules. The powder is then macerated for 12 hours in 0·25–0·3% $NaOH$, causing the gluten and fibre to swell and rise to the surface, leaving a thick suspension from which the starch is recovered by centrifuging and settling.

Warth and Darabsett (Pusa Bull. 1914, No. 38) found that dilute alkali rapidly disintegrated polished rice, whereas unpolished rice was not affected. They suggested that this action of alkali might be used as a basis for testing the quality of starch in rices.

Steinbarger (Cereal Chem. 1932, **9**, 317) tested the cooking quality of eight varieties of domestic rice by a standardised method and suggested that the diversity of cooking times made the mixing of varieties undesirable. Sugimoto, *et al.* (Imp. Jap. Inst. Nutrition; Bull. Soc. Hyg. aliment, 1927, **15**, 481, 524) also record the effect of cooking methods.

Amylase.—Venkata Giri and Sreenivasan (J. Indian Inst. Sci., 1934, **17a**, 127; Science, 1935, **81**, 343) have done valuable work on the amylases of rice, etc., and have devised a simple qualitative method for their differentiation. The method consists in adding a small drop of enzyme solution to a thin layer of agar gel impregnated with starch in a petri dish and allowing it to diffuse for 28 to 48 hours at the laboratory temperature. At the end of the period a dilute solution ($N/200$) of iodine is poured on the plate, and allowed to remain there for about 2–3 minutes, until the colours of all the diffusion zones come out clearly. A deep blue background with a round diffusion field at the centre is formed. The central diffusion field is coloured violet in the case of β-amylase and colourless in the case of α-amylase. Amylases which contain mixtures of both the components produce a central colouring diffusion field with a violet or green and violet zones surrounding it, depending on the nature of the amylase and starch used. They show that the resting rice grain contains two amylases with different p_H optima. One, of optimum p_H 4·6, behaves like a pure β-amylase, and another, of optimum 7·0, behaves like a pure α-amylase in the hydrolysis of amyloamylose. These two enzymes can be obtained in an active state by extraction with phosphate buffer ($M/15$) at p_H 7·0. The work of Venkata Giri and Sreenivasan does not agree with the view put forward by Ohlson and co-workers that the amylase arises only during the germination of the seed (Nordh and Ohlsson, Z. Physiologischemie, 1931–32, **204**, 89; Ohlsson and Uddenberg, *ibid.* 1933, **221**, 165; Ohlsson and Edfeldt, *ibid.* 1933, **221**, 174; Waldshimdt-Leitz, Reichel, and Purr, Naturwiss. 1932, **20**, 254; Myrback and Myrbrack, Biochem. Z. 1933, **258**, 158; Samec and Waldschmidt-Leitz, Z. Physiol. Chem. 1931, **203**, 16).

Karmakar and Patwardhan (J. Indian Inst. Sci. 1931, **14A**, 4) obtained rice-malt amylase by extracting the sun-dried malt powder, obtained after paddy had been steeped for 4 days at 24°–25° and allowed to germinate, with 0·6% aq. $NaHCO_3$, and precipitating with alcohol. They found it to be less than a quarter as active as wheat amylase. It loses its activity after 15 days' continuous dialysis. The optimum temperature is 60°.

Amylosynthease.—Minagawa (Bull. Agric. Chem. Soc. Japan, 1935, **11**, 62) obtained from rice an amylosynthease which differs from that obtained from yeasts. It can be precipitated by ethyl alcohol or acetone from aqueous solution as a highly active powder. A similar enzyme has been detected in corn, millet and potato. The amylosynthease is inactivated by acids, alkalis, $HgCl_2$, and heat, it is not reactivated by neutralisation, H_2S, or cooling. When it is precipitated by $CdCl_2$ and treated with $(NH_4)_2SO_4$ its enzymic activity is restored. Glutinous rice gives an amylosynthease with optimum p_H of 6·7–6·8. The preparation of this is described by Minagawa (*ibid.* 1933, **9**, 547, 549).

Catalase.—Winton (*op. cit.* 151) states that Sampietro (Giorn. risicoltura, 1923, **13**, 133) obtained results indicating that there is a relation between the germinative capacity and the catalase content. Borasio (*ibid.* 1924, **14**, 143) was unable to find any such relation although he states that other enzymes may influence germination. Higochi (Imp. Jap. Inst. Nutrition, Bull. Soc. hyg. aliment. 1927, **15**, 481, 524) determined catalase as follows: 100 grains were ground and suspended in 100 c.c. water. The mixture was filtered, 25 c.c. were kept for one hour at 25° after admixture with 10 c.c. neutral H_2O_2 (0·05%) and the excess was titrated with permanganate after addition of sulphuric acid. He described the variations of catalase, peroxidase, and oxidase with the quality and origin of the rice.

Protease.—Giesen (Inaug. Dis. Bern, 1909) found 0·70% calculated as trypsin.

Lipase.—Browne (*l.c.*) first showed that the rapid deterioration of rice oil was due to this enzyme.

Oxidase and Peroxidase.—Noguchi (J. Sci. Agr. Soc. Japan, 1923, **245**, 115) carried out experiments on the effects of storage on the enzymes. Oxidase did not change, but peroxidase decreased abruptly after one year. Kondo and Okamura (Ber. Ohara Inst. landw. Forsch. 1931, **5**, 57) experimenting with the green-coloured rice "Aomai," and the action of various coloured

lights on the chlorophyll content, found that there was also a reduction in the activity of the catalase and peroxidase present.

Yamagishi (J. Agric. Chem. Soc. Japan, 1934, 10, 496, 502) says that the "starch liquefying enzymes" of padi and brown rice showed optimum activity at p_H 4 1–4 3 and 36°–42°C. They were absent from polished rice. He found that an aqueous extract of a mixture of polished rice and papain liquefies starch and suggested that zymogen may occur in polished rice

Bishop and Teik (Malay. Agric. J. 1928, 16, 14) give an account of the process used by the Chinese in Malaya for the manufacture of "Samsu" from rice The process depends on the utilisation of a mould (*Amylomyces Rouxii*) containing a ferment which converts moist starch into alcohol. The mould is added in the form of "rice cake" consisting of rice starch, soya beans, clay, vegetable tissue, and variable amounts of *mucors* and yeasts. The rice is boiled, allowed to cool, and the rice cake roughly mixed into it in the proportion of 3 parts of rice to 1 part of rice cake. The mixture is placed in earthenware jars with water and left for 27 days. Distillation is carried out in a primitive apparatus. A yield approx. 54% theoretical is obtained. "Moti" is a form of rice cake made by steaming and pounding glutinous rice. Maeda and Syôzi (Sci. Papers Inst Phys. Chem Res. Tokyo, 1931, 16, 261) investigated the conditions under which this material hardens to a stone-like mass. They contend that it is due to the evaporation of water from the surface and the binding of free water in the interior of the mass by starch granules. The hardening of "moti" is analogous to the setting of cement. Both during cooling and heating, "moti" shows a transition point at 63 5°C. This may be connected with the water of crystallisation (*cf.* St. V. Náray Szabó, Z. physikal. Chem. A. 1930, 151, 420).

MINOR ELEMENTS IN RICE.—*Aluminium.*—1·4 mg. per kg dry matter (Bertrand and Lévy, Compt. rend 1931, 192, 525).

Copper.—Dry, hulled rice, 6 4 mg. per kg. (Guérithault, Compt. rend. 1920, 171, 196); rice polish (dry), 8 0 mg. per kg. (McHargue, J. Amer. Soc. Agron. 1925, 17, 368); rice (1) (air-dried), 1·32 mg per kg., rice (2) (air-dried), 1·66 mg per kg. (Quartaroli, Ann. Chim. appl. 1928, 18, 47).

Iron.—Sherman (U.S. Dept. Agric. Off. Exp. Sta. 1907, Bull 185, 51):

	Fe (mg per kg dry matter)
Polished rice	6
Rice—Japanese	9
Rice—meal	19

Winton (*op. cit.* 152, 153), quotes the following figures:

Manganese

	Mn (mg per kg. dry matter).
Polished rice	10
Rice polish	112 (McHargue[1])

[1] *l c.*

Zinc:

	Zn (mg per kg dry matter)
Polished rice	7 5
Rice polish	7 6 (McHargue)
Unshelled Japanese rice	14·7 (Birckner[1])
Polished rice	2 9
Rice bran	33 3 (Bertrand and Benzon[2])

Arsenic:

	As (mg per kg dry matter)
Rice kernel	0 07 (Jadin and Astruc[3])

[1] J Biol Chem 1919, 38, 191
[2] Bull Soc hyg aliment 1928, 16, 457.
[3] Comp rend. 1912, 155, 291.

UTILISATION OF PADDY HUSK OR HULLS—In Siam, and to a smaller extent in Italy, the power to run the mills is obtained by burning the hulls in furnaces. The insoluble portion of the ash of paddy husks is largely silica, and Mongeot (Giorn. Chem. Ind. Appl. 1930, 12. 74) suggests that this silicious ash could be used in the glass industry in Italy, the annual production being 16,900 tons.

Dry distillation of the husks gives a carbon of low density, acetic acid, propionic acid, furfur aldehyde, phenols and cresols The husks are rich in cellulose and might be used as a source of industrial alcohol According to Harding (Ind Eng. Chem. 1928, 20, 310), a pure edible cellulose may be prepared from the hulls of rice and other cereals by boiling with strong soda and subsequent hydration treatment to reduce the cellulose to the proper physical condition, for raising the roughage content of breakfast foods A typical cellulose consists of α-cellulose, 72%, hydrated cellulose 25%, ash 0 8%, with copper number 8 7.

Sauerbrey Maschinenfabr. A.-G. (G.P. 456891) describes an apparatus for distilling rice husks.

Rankin has patented a method for oxidising the carbon compounds to oxalic acid (U.S.P. 1520885). Finely divided rice hulls are fed in at the top of a cylindrical vessel containing strong nitric acid. The rice hulls are rapidly oxidised, with formation of oxalic acid.

The husks may also be used for making paper Dickie and the British Burmah Petroleum Co, Ltd, have patented a process for the manufacture of waterproof board, utilising the fibre from paddy husks (E.P. 239970).

Morgenier (U.S.P. 1570389) suggests boiling the rice hulls for 2 hours with $NaOH$ at 10°Bé (*d.* 1 07), removing the liquor and beating the residue to a pulp. Puttaert (U S P. 1588335) prepares a pulp, using a more dilute solution of $NaOH$ and boils for 6–8 hours at a pressure of 20–80 lb. per sq in. Utaka (Rep. Osaka Ind. Res Lab. 1925, 5, [16], 1), by hydrolysis with steam under a pressure of 100 lb. to the square inch, obtained a yield of 9–10% furfuraldehyde using HCl as a catalyst. Other products were 0 03% acetaldehyde, 0 07%, "volatile organic acid," 2% sugar, and a trace of methyl alcohol.

RICE STRAW.—Rice straw has little value as a fodder. Analyses of straw (1) from a good harvest, (2) from a poor harvest, were made by Takeuchi (Bull Coll. Agr. Tokyo, 1908, 7, 619):

Rice Straw from India.

Analysed at Rothamsted Experimental Station in *Fermentation Laboratory*.

No.	Type of Soil.	Percentage on Dry Matter. Pentosans.	Ash.	Nitrogen.
1.	Marshy	26·54	17·2	0·41
2.	Salty clay	22·4	—	—
3.	Hard clay	25·2	—	—
4.	Medium clay	20·9	—	—

Rice Straw (India).

C. N. Acharya (Biochem. J. 1935, 29, 1459).

Constituents.	%
Cellulose (deducting xylan contained)	32·82
Xylan associated with cellulose . .	11·73
Xylan not associated with cellulose .	9·31
Lignin (direct)	10·67
Protein	2·88
Ash	17·50
Alcohol-benzene extractive . . .	3·05
Moisture	8·40
Total . . .	96·36

Composition of Rice Straw.

R. D. Rege ("Annals of Applied Biology," 1927, XIV, 1).

	g.
Dry matter . . .	100
Organic matter . .	82·67
Ash	17·33
Cellulose	45·46
Starch	0·7
Dextrose	0·65
Invert sugar . . .	0·6
Pentosans . . .	24·6
Lignin	10·06
Total nitrogen . .	0·41

According to Iwata (J. Dept. Agric. Kyushu, 1926, 1, 217) the digestibility of rice straw may be increased by treating with solutions of $NaOH$ (0·75–1·5%) or boiling with milk of lime (CaO 1%) for 3 hours. The quantity of lignin is reduced and the starch value of the dry matter may be increased from 20% to 53–58%.

Taketomi (J. Soc. Chem. Ind. Japan, 1926, 29, 43) obtained sugar and alcohol from rice straw. The straw was heated with 1% H_2SO_4 at about 134° for 30 minutes in an autoclave. Neutralised with $CaCO_3$, the liquid concentrated and fermented with yeast (race XII). The yield of sugar was about 15% and of alcohol about 5·4% of the dry matter used.

Patwardhan (J. Indian Chem. Soc. 1930, 7, 531) found that the yields of reducing sugar obtained by hydrolysis of Bangalore rice straw are proportionately increased by increase of the concentration of the sulphuric acid used from 2% up to at least 6%, these results being at variance with those of Thaysen for Burma rice straw. ("Fuel for Motor Transport," H.M. Stationery Office, 1927.) *B. acetoethylicus* may be trained to ferment pentoses (such as are obtained by processes similar to the above) at concentrations up to 7%, but yields of alcohol and acetone, which are somewhat variable (*cf.* Thaysen and Galloway, Ann. Appl. Biol. 1928, 15, 392), generally decrease continually as the concentrations of sugar are increased above 3%. Change of nutrient mixture from ammonium phosphate and peptone to combinations of ammonium nitrate, disodium hydrogen phosphate, and yeast water does not materially affect the yields. The presence of small quantities of hexoses, *e.g.* dextrose, facilitates the growth of the bacterium and fermentation of the pentoses.

Straw as a Raw Material for Making Paper.—Reyes and Cruz (Philippine J. Sci. 1929, 38, 367) recommended the use of rice straw as raw material for the manufacture of paper and compare it favourably with the weed *cogon grass*. Rice straw requires only about 8% of soda, whereas cogon needs 20% to produce a bleachable pulp, and gives a higher yield. For cardboard, cogon requires digestion with 4% soda, and gives a yield of 51·5% of pulp, whilst rice straw requires only 2% of caustic soda and gives a yield of 55·4%.

Kumagawa and Shimomura (Z. angew. Chem. 1923, 36, 414) compared rice straw with bagasse for the manufacture of paper pulp. In spite of a much higher ash and silica content, rice straw was more easily decomposed than bagasse, but the yields were smaller. The high ash content of the resulting fibre did not affect adversely the quality of the paper.

Storage of Rice.—Jack and Jagoe (Malay. Agric. J. 1930, 18, 447) say that under rat-proof and well ventilated conditions rice may be stored in good condition for two years, but should be winnowed before use. It can also be stored in airtight containers for at least 2 years if fumigated with CS_2 (5 c.c. to 18 litres of rice). This fumigant imparts a yellow tinge to the uncooked rice, but does not affect its edibility. The vitamin B content of rice does not deteriorate on storing.

Kondo (Ber. Ohara Inst. landw. Forsch, 1926, 3, 153) studied the variations in temperature of stored, hulled rice in relation to the air temperature and the changes in water content and other properties of the rice during storage.

Kondo and Okamura (*ibid.* 1929, 4, 1) give data to show the superiority of storing rice in airtight vessels, or in CO_2, over the normal method used by the Japanese farmer of storage in straw bags. The same authors (*ibid.* 1929, 4, 127, 147, 163 ; 1932, 5, 375) conclude that the grains of unhulled rice are as hygroscopic as hulled (brown) rice, although the husk itself is less hygroscopic than either.

Storage of rice in the presence of $CaCl_2$ minimises the loss of germinative capacity with age (Kondo and Okamura, *ibid.* 1931, 5, 221; 1935, 7, 99). There was no specific relationship observed between loss of germinating power and destruction of the catalase. Kondo and Okamura (*ibid.* 1932, 5, 395, 407, 413 ; 1934, 6, 149, 175) continuing their studies on storage conditions found that the germinative power, vol.-wt. per 1,000 grains, H_2O absorbing power, and swelling capacity of stored grain decrease with time. Provided insect attack is avoided, changes in chemical composition were small in a period of 2·5 years. The relative vitamin B

contents during the first 4 years of storage were 100, 92, 82, 56, and 23 respectively. The safe limit of storage of hulled rice in straw bags is 2 years. Conditions causing loss of germinating power in stored rice (*e g.* high temperature and moisture) also favour loss of vitamin B Airtight storage minimises losses. Prolonged *storage of sun dried rice (11–13% H_2O) did not* greatly affect its physical condition or chemical composition. Little or no peroxidase activity was retained, but the catalase activity and vitamin B contents were relatively high.

Kondo and Okamura concluded that rice may be safely stored in sealed containers, or in CO_2 for several years, if the H_2O content is 10–12%. With >14% H_2O deterioration increases rapidly with rising water content Catalase activity of hulled rice decreases after 3 5 years *in storage, or earlier if with* >13% H_2O. Glucose and dextrin contents decreased rapidly. No change in vitamin B activity occurred during storage for 5 years with 10–12% H_2O. In unhulled rice, stored for 46–84 years in granaries (14–14 9% H_2O), there was a decrease in fat and, in some cases, in sugar content, but no change in protein, *starch or ash. The activity of peroxidases* catalase and urease disappeared, that of diastase and reductase declined considerably, but lipase was not affected. Colour and flavour deteriorated (Kondo and Okamura, Proc Imp Acad Tokyo, 1934, 10, 528) Storage in airtight containers of rice having 13% of H_2O involved minimum changes in swelling capacity, flavour, and germinative capacity In the range 10–16% H_2O changes in carbohydrate, protein, and ash contents were insignificant Fat, *crude fibre, and p_H declined in grain stored with* >14% H_2O. Catalase activity decreased with rising H_2O content Vitamin B remained constant with 10–12%, but decreased with >14% H_2O. Storage in CO_2 had no beneficial effect (Kondo and Okamura, Ber Ohara Inst landw Forsch, 1934, 6, 331)

Rice with an initial H_2O content of 14 2% lost 1 5% *during storage with $CaCl_2$, retained* good quality and a germinative capacity of 93–99%; with 16 9% initial H_2O content, quality was less good and the germinative capacity fell to 38–54%. In both cases the lower parts of the containers were less effectively desiccated and the rice was inferior.

VITAMIN B.—The study of "beriberi," a disease characterised by severe nervous disorder, occurring principally among the populations of the East, and avian polyneuritis, the physio*logical equivalent of human "beriberi,"* proved that they were caused by a diet restricted to highly milled or polished rice. "Beriberi" and polyneuritis can both be cured by a diet of unmilled or home-milled rice, or by restoring to the diet the valuable constituents (embryo and pericarp) removed in the milling The diseases have been proved to be due to the removal of *vitamins from the rice, viz. the vitamin B com*plex. The largest quantity of the anti neurotic factor is found in the embryo or germ, the bran (pericarp and aleurone layer) contains less, while the endosperm is entirely deficient in this substance. Thus the deficiency of polished rice is due more to the removal of the embryo than to the actual "skinning" of the grain. Beriberi can be cured by an alcoholic extract of the bran or rice meal.

The normal composition of rice polishings (darak), from which the anti beriberi concentrates (tiki tiki extracts) are made, is given by *Hermano and Amdo (Philippine J. Sci. 1933, 50,* 189) as protein 13 81, fat 16 96, carbohydrates 38–36%

Suzuki *et al.* (Biochem. Z. 1912, 43, 89) first isolated the anti neurotic principle from the alcoholic extract of rice bran and polishings and called it *oryzanin*, not to be confused with the glutelin oryzenin, p 492. Oryzanin is soluble in water and dilute alcohol, and is precipitated by some of the usual protein reagents (*see* B_1 VITAMIN, Vol I, p. 583)

TOXIC SUBSTANCES PRESENT IN POLISHED RICE —Williams (Biochem. J. 1927, 21, 1349) stated that rice bran and meal although capable of preventing avian polyneuritis when incorporated in a basal diet consisting of polished rice, are distinctly harmful to pigeons when fed, as the exclusive diet This harmful effect varies with different samples

Destruction of Vitamin B—Rosedale, *et al.* (Biochem J 1928, 22, 1362) found that the antineuritic vitamin of an extract of rice polishings is destroyed by fermentation and by sterilisation Van Veen's (Geneesk Tijds Ned Ind 1934, 74, 672) experiments showed that washing and steaming had little effect on unpolished rice, at least half of the vitamin B remaining intact Quite short washing had a great effect on slightly polished rice, whilst a single steaming did not cause much change

Van Veen and Koks (Geneesk. Tijds Ned. Ind. 1934, 74, 482) state that exposure to SO_2, up to 3–4 5% conc. for almost 3 hours (the Clayton process) caused a loss of vitamin B_1 depending on the moisture and degree of milling of the rice, also on the method of packing When the rice was packed in small sacks the loss of vitamin B_1 in dry paddy was negligible, *that in lightly milled "silver skin" rice* was over 30%, and that in half milled rice 50%. When silver-skin rice was packed in large sacks the loss of B_1 was negligible.

Kondo (Proc Imp Acad. Tokyo, 1929, 5, 159) proved that rice preserved for 4 years in CO_2 in airtight containers showed no loss in germination, food value, and vitamin B content when compared with freshly harvested rice, whilst rice kept in straw sacks showed a total loss of vitality.

PHOSPHORUS-ORGANIC COMPOUNDS.—Phosphoric acid occurs in organic combinations with inosite in the seeds of many plants, including rice, the most important of these compounds is known as phytin. Thompson (J. Agric. Res 1915, 3, 425) records the following figures for phosphorus. rice bran 2 291%, unpolished rice 0 321%, polished rice 0 140%. He deter*mined the phytin by extracting* 100 g. of the sample with 0 2% HCl and precipitating with alcohol; washed with 50% alcohol and then with ether and dried at 105°C Bran contained 8 22% phytin. None was obtained from polished rice. According to Bernadini

(Atti R. Accad. Lincei, 1911, 21, 283) the phosphorus is distributed as follows:

Form of combination.	Embryo. %	Whole grain. %
Lecithin	0·04	0·003
Lecithide	0·22	0·018
Phytin	5·15	0·436
Nuclein	0·76	0·502
Inorganic	0·04	trace

Borasio (Giorn. risicolt, 1929, 19, 131) found 2·4% of phosphorus of which phytin accounted for 1·7% and lecithin 0·003%, in " gemma " or rice embryo. Kimura (Bull. Waseda App. Chem. Soc. 1933, 19, 14) gives the composition of " oryza-nucleic acid " from rice embryo: N 14·42%, P 6·81%. On hydrolysis he obtained pentose, guanine, adenine, and uracil, but not cytosine.

Iwata (Proc. Imp. Acad. Tokyo, 1930, 6, 212) extracted from polished rice 0·2% of a toxic compound, *lysolecithin* ($C_{24}H_{50}NPO_7$), by repeated digestion with 94% alcohol. The compound is lævorotatory, $[\alpha]_D^{20}$ —4·52°, softens at 100°, and decomposes at 262°–264°. On hydrolysis it yields palmitic acid, choline, and glycerophosphoric acid.

Belfanti (Arch. Ital. Biol. 1931, 85, 190; Chem. Zentr. 1931, II, 2029) calls attention to the lack of phosphatase in polished rice which would decompose toxic lysolecithins. This is important in connection with the onset of avitaminosis. Marotta and Calo (Annali Chim. Appl. 1932, 22, 763) extract the phosphorus-organic compounds with 0·25% HCl, followed by neutralisation with NaOH.

RICE PRODUCTS AS FEEDING STUFF.—Warrington's (" Chemistry of the Farm," 1919, p. 130) classic figures for the composition of rice meal are:

Water. %	Albuminoids. %	Amides. %	Fat. %	Sol. carbohydrate. %	Fibre. %	Ash. %
10·3	11·3	1·0	12·0	47·8	8·6	9·0

Digestibility (Warington, *l.c.* 144):

Cattle, Sheep, and Goats.

Digested for 100 of each constituent supplied:

Total organic matter.	Nitrogenous substances.	Fat.	Sol. carbohydrate.	Fibre.
75	63	85	86	26

Peroni (Giorn. Agric. Domenica, 1932, 42, 12, 151; Bied. Zentr. 1933, A–3, 434) after, feeding experiments with cows and store cattle, suggests that rice bran should be oven-dried to prevent rancidity (*cf.* West and Cruz, Philippine J. Sci. 1933, 52, 1) and found that broken rice tends to produce firmer fat than bran. Honcamp and Pfaff (Landw. Versuchs-Stat. 1924, 102, 243) describes digestibility trials with sheep fed on a basal ration to which various mixtures of rice-meal and ground rice-husk were added. The digestibility of the mixtures steadily decreased as the proportion of husk increased.

Tirol (Agric. J. Fiji, 1933, 6, 41) records analytical data for coarse and standard rice bran. With pigs the former produces poor and the latter good growth when fed with a supplement of salt and lime.

Martin (Arkansas Agric. Exp. Sta. Bull. 1934, 303) contends that for the satisfactory fattening of pigs on mixed rations containing rice, bran and other by-products, the process must be finished by the provision of hard fat-producing foods. Smith (*ibid.* 1934, 304) recommends the use of rice products for feeding poultry if supplemented with a vitamin A concentrate. Hermano (Philippine J. Sci. 1933, 51, 567), by feeding experiments on young rats, concluded that Mancasar rice, although containing less protein than the three other varieties tested, has the highest nutritive value. Nagaska (J. Agric. Chem. Soc. Japan, 1933, 9, 1365) says that fresh, unpolished rice is more readily digested by rats than material heated to 150°C. or steamed. Sheets and Semple (U.S. Dept. Agric. Misc. Publ. 1931, 132) record the analyses of milling products and their uses in various livestock rations.

Some of their findings are: for *milch cows* rice bran is worth, in digestible nutrients, about 5% more than wheat bran and 75–80% as much as ground corn, but rice polish is superior to ground corn. For fattening *cattle* brewers' rice and rice polish have practically the same feeding value, but in the feeding of *hogs* the quantity must be limited on account of its tendency to produce soft pork. For *horses* and *mules* good results have been obtained with 8 lb. of ground rough rice, as has 1–1½ lb. cottonseed meal daily per 1,000 live weight. In general rice bran and rice polish should be fed with barley or corn or supplemented by some variety of oil cake or a similar food rich in protein.

PHYSIOLOGICAL CHEMISTRY OF RICE PLANT.—Davidson and Chambliss (Science, 1932, 75, 294) analysed five varieties of Chinese rices grown on soil continuously cropped for centuries, and four rices grown under the American method of cropping. There were no marked differences between the two groups in ash, N, P, K, Ca, Mg, and S contents. Professor King, in his book " Farmers of Forty Centuries," contends that the Chinese and Japanese cultivators have long been applying quite as much of the three main plant foods (N, P, K) as are removed by the crop. It is true that rice in China and Japan is grown under continuous cropping but not without restitution of plant food.

In a private communication, M. R. Ry. K. Ramiah reports on the formation of starch in the developing rice kernel thus: " In the early stages of grain development the starch is present in the ovary wall and pericarp layers and gradually infilters into the endosperm region. . . . Starch appears in the embryo a little later than in the endosperm. As the grain matures the starch gradually disappears from the pericarp but remains longer in the embryo region. Starch was first noticed in the endosperm on the fourth day after anthesis, whereas Shinichi Terada (J. Coll. Agric. Sapporo, 1927, 19, 245) observed it to have taken place on the eighth day."

Tao (Bull. Chem. Soc. Japan, 1930, 5, 64, 69) studied the chemical changes of the starch during germination.

Loss of weight occurs during germination, the chief decrease occurring in the starch content, whilst the amount of reducing sugars and soluble polysaccharides increases, but not sufficiently to account for the starch destroyed Fat remains constant. Sahasrabuddhe and Kibe (J. Univ. Bombay, 1934, 3, 121) studied the seed from the time of sowing until it was depleted of its food constituents. The seed absorbs water rapidly and retains a high moisture content throughout. Crude fibre and ash are little utilised, and 90% of the proteins are used up. The ether extract increases for some time, due to formation of fatty acids. The soluble carbohydrates are first converted into glucose and finally utilised by the growing parts of the new plant. An amylohydrolytic enzyme is present in the germinating rice seed.

Dastur and Desai (Ann Bot. *1935, 49, 53*) investigated the aerobic and anaerobic respiration of rice seeds. In rice germinating in air the total sugar content at any time is directly correlated with the output of CO_2. When germination occurs in an atmosphere of nitrogen no hexoses occur at any stage, sucrose is present only in small amounts, but ethyl alcohol is formed In aerobic and anaerobic respiration the CO_2 produced is more than equivalent to the carbohydrates lost. The excess is probably derived from the oxidation of organic acids formed during protein synthesis Tadokoro (J. Coll Agric Sapporo, 1927, 20, 333) studied the chemistry of ripening rice grain. During the ripening process the non protein decreases and the protein increases. The composition of the oryzenin changes by a decrease of mono-amino and an increase of di amino nitrogen The degree of polymerisation of the starch decreases in the middle of the ripening period and then increases later.

Tadokoro and Abe (J Fac. Agric. Sapporo, 1930, 27, 349) found that during ripening the ash and phosphorus decreased at first. The total nitrogen was unchanged, but the ratio of protein to non protein N increased The water soluble protein decreased, whilst the NaCl and alcohol soluble groups increased The amount of dextrose formed by acid hydrolysis was maximal before complete ripeness At the same period the rotatory power of the acetylated starch was maximal and its acetyl content minimal.

Plant Food Requirements of Rice.—Rice takes up nitrogen in the form of ammonia, amides and nitrates, but Nagoaka (Bull. Coll. Agric. Tokyo, 1904, 6, 285) found that upland rice (hill rice) which grows normally in aerated soil needs less ammoniacal nitrogen than does swamp rice. Espino (Phil. Mag. 1920, 16, 455), experimenting with water cultures, showed that some nitrate was necessary to even the youngest rice plants. In the absence of nitrates the tips of the leaves always died. Gericke (Soil Sci. 1930, 29, 207) adversely criticised Espino's work. He stated that the nutrient requirements of rice cannot be determined by growth to maturity in complete nutrient solutions. Under these conditions the plants absorb more mineral matter than is utilised for growth purposes. Iron is the first element to become a limiting factor in growth. Mitra and Phukan (Proc. XV. Ind Sci Cong 1928, 167) reported that maximum root development was associated with a water-culture in which 0 5 of the total osmotic concentration was due to KH_2PO_4, 0 2 to $MgSO_4$, and 0 3 to $Ca(NO_3)_2$, and minimum root development with 0 3, 0 2, and 0·5 respectively.

Mitra and Phukan (Agric. J. India, 1929, 24, 109) continued their experiments with rice seedlings using water cultures of p_H varying from 3 0 to 8 4. The total length of root produced was again taken as a measure of plant growth. The maximum growth was obtained at p_H 7·9. At p_H 6 0 growth was below normal; at p_H 3·9 the culture solution was strongly toxic, and at p_H 3 3 growth was inhibited. Evidence is presented that toxicity was due directly to the hydrogen ion concentration and not to the titratable acidity or alkalinity. Dastur and Malkani (Indian J. Agric. Sci. 1933, 3, 157) found that from solutions of ammonium salts the rice plant absorbs more NH_4 ions than anions. After 8 days the p_H of the solution drops From nitrate solutions a similar phenomenon is noticed, but in the later stages the NO_3 ion is absorbed in greater proportion than the cation and so the p_H of the solution rises These results are quoted as an explanation of the work of Kellner (1884) and others who observed that the rice plant needed ammoniacal nitrogen in the early stages of growth and nitrate nitrogen in the later stages

Dastur, in collaboration with Kalyani (Indian J. Agric. Sci 1934, 4, 803), continued his investigations on the nitrogen intake of the rice plant with regard to (*a*) changes in the p_H value of the soil and plants when fertilised with ammonium sulphate, sodium nitrate, and a mixture of the two salts; (*b*) p_H of the water culture solutions before and after rice seedlings, 7 days old, had remained in them for a fixed period, and p_H of the plant juices; (*c*) the iso electric point of the proteins in the protoplasm of the roots and leaves. The results show that the iso-electric point of the plant-tissue lies between p_H 4 1 and 4·4. In the early stages of growth the p_H values of the roots lie on the alkaline side of the iso electric point of their proteins and therefore the latter will combine more readily with the basic ions than with the acidic ions. As the ammoniacal nitrogen is in form of the basic ion it is absorbed in the earlier stages of growth while the nitrate ions, being acidic, are very little absorbed. The reverse is the case during the later stages of growth. The p_H of the roots is on the acidic side of the iso-electric point and therefore the proteins of the roots absorb acidic ions in preference to basic ions. Thus the absorption of nitrate nitrogen takes place while the absorption of the ammoniacal nitrogen diminishes.

Jacobson (J. Amer. Soc. Agron. 1925, 17, 583) also studied the changes of p_H of water culture solutions with rice. Four solutions of different salt compositions were employed. Previous to the test the cultures were grown in their respective solutions, which were renewed every 3½ days, for 100 days. On the hundredth day fresh solutions were supplied to each culture.

after which samples of these were taken at different intervals for 3 days and analysed for total N and tested for p_H:

(1) 80% of total N was gradually removed during the 3 days of the experiment.

(2) The p_H changed from 5·0 to 3·0 in one 3-day period.

(3) The decrease in p_H, although gradual, was more marked after photosynthesis had ceased.

(4) CO_2 from roots was probably the main cause of this decrease.

(5) The taking up by the rice plants of cations of salts having SO_4 anions, resulting in the formation of H_2SO_4, was only a partial cause.

Ishizuka (J. Agric. Chem. Soc. Japan, 1934, 10, 128) after experimenting with sand cultures on the adsorption of N, P, K, concluded that K is required throughout growth, and N up to the ninth week. P is necessary for the first 3 weeks or for the whole period after the third week, the former being better.

Investigating the adsorption of Ca and Mg by rice plants in water cultures, Ishizuka (*ibid.* 1933, 9, 1022) found that the CaO/MgO ratio was 3 : 1 at first but gradually approached 1 : 1. Gile and Carrero (J. Agric. Res. 1915, 5, 357) analysed the ash of upland rice at different stages of growth. They found that the amount of potash, phosphoric acid, and sulphur in the ash of the whole plant above ground decreased with the age of the plant, while silica increased and N in the dry matter decreased with age. The percentages of iron in the ash of the green leaves and straw decreased with the age of the plant, while the iron content of the above ground portions of the plant remained constant after 26 days' growth. The total ash varied, thus:

Days.	Ash—% on dry matter—whole plant above ground.
18	17·75
48	22·21
103	14·99
123	14·96

Gile and Carrero's conclusions do not agree with the findings of Herrero (Actes du Congrès Internat. de Riziculture Valencia, 1914, 128), with regard to potash. Treating the plant's maximum content as 100, Herrero tabulates his results as follows:

	Seed-bed.	Growth.	Flowering.	Maturing.
Duration	..	52	22	22 days
Nitrogen	0·94	74·90	85·51	100
Phosphoric acid	1·01	75·80	93·10	100
Potash	0·81	74·84	100·00	48·60
Dry weight	8·20	70·80	84·00	100

Kelly and Thompson (Hawaii Agric. Exp. Sta. 1910, Bull. 21) made a full investigation of the composition of the rice plant at various stages of growth both with and without the use of fertilisers. The following tables show the composition of the dry matter of the plants on the untreated control plots.

COMPOSITION OF DRY MATTER.

Just before Formation of the Flower.

	Roots. %	Vegetative portion. %	Total plant. %
Nitrogen	1·14	2·43	2·17
Potash	1·86	2·51	2·38
Phosphoric acid	1·10	0·89	0·93
Lime	0·44	0·19	0·24
Magnesia	0·51	0·24	0·29
Carbohydrates	29·94	30·36	30·27

At Time of Full Flower.

	Leaves. %	Roots. %	Stems. %	Panicles. %	Total plant. %
Nitrogen	1·80	0·68	0·63	1·45	1·15
Potash	1·89	0·93	1·77	0·72	1·49
Phosphoric acid	0·63	0·91	0·74	0·68	0·71
Lime	0·36	0·42	0·12	0·12	0·22
Magnesia	0·20	0·39	0·21	0·27	0·24
Carbohydrates	24·00	35·09	44·08	33·01	34·86

At Maturity.

	Roots %	Stems %	Leaves %	Chaff %	Grain %	Straw %	Total plant %
N	0·63	0·50	0·86	0·52	1·36	0·58	0·90
K_2O	0·58	2·18	1·30	0·96	0·39	1·69	1·10
P_2O_5	0·76	0·26	0·28	0·43	0·98	0·30	0·61
CaO	0·70	0·10	0·69	0·15	0·02	0·24	0·19
MgO	0·83	0·08	0·21	0·26	0·27	0·13	0·24
Carbohydrates	34·55	29·61	18·53	18·02	79·66	24·36	47·32

Some of the Conclusions.—Fertilisation with nitrogen either with or without minerals greatly increased the growth of the rice at all periods of its development.

The percentage of N was considerably increased by N fertiliser and was still further increased by the application of minerals in addition to nitrogen. The percentage of N in the mature plant was not materially changed by the fertilisers.

The plants receiving N, P, K contained at every period of growth a higher percentage of potash.

The percentage of P_2O_5 at the first period was influenced slightly by the fertilisers. In subsequent growth no difference in the phosphoric

acid content was found. The Ca and Mg in the total plant were not greatly different at the several periods of growth. The Ca at maturity is stored in the leaves while the Mg migrates to the grain.

The hydrolysable carbohydrates vary inversely with the percentage of N absorbed. *Reducing sugars were found at all stages of* growth and were greatest at the first period.

Sucrose.—First period, traces only, second period, 10 38% in stems. At maturity this had been largely converted into starch.

Chlorosis—According to Willis and Carrero (J. Agric. Res. 1923, 24, 621) nitrogenous fertilisers may cause chlorosis in rice. The basic residues of sodium and calcium nitrates may precipitate iron in a form unassimilable by plants, whereas the acid residues from *ammonium sulphate tend to retain iron in a* soluble form. The inferiority of nitrate fertilisers compared with ammonium salts for *rice is ascribed to chlorotic effects rather* than, as previously believed, to the toxic effect of nitrites produced by reduction. Metzger and Janssen (J. Agric. Res 1928, 37, 589) say that rice plants become chlorotic when they suffer from a lack of available N, particularly ammonia, in the early stages of growth.

Kapp (Arkansas Agric Exp Sta. Bull 1932, No. 277) reported that chlorotic plants occurred on soils receiving nitrogenous fertilisers but no lime. Addition of iron salts did not always effect *an improvement. He suggests that chlorosis* is the result of an unsuitable Fe . Mn ratio.

Miyake and Adachi (J. Biochem. Japan, 1925, 5, 321) found that nitrogenous fertilisers lowered the hydrogen ion concentration of the juice of the rice plant, the effect being greater when applied in conjunction with P and K. On the other hand, P alone increases the hydrogen ion concentration, the effect being weakened by K or N. In the first period of growth K decreases and in the second period increases the *hydrogen ion concentration of the juice.*

Belval (Comp rend 1928, 186, 781) showed that the leaves of the rice plant contain more *sucrose and less reducing sugars than the stems.* Probably the only reducing sugars present are the inversion products of sucrose. The amount of sugars increases towards the autumn. According to Soriano (Philippine Agric 1934, 23, 295), leaves of plants fertilised with ammonium sulphate contained more chlorophyll and less ash than those receiving nitrate of soda. The dry matter was equal in both cases. Root excretions of grasses and weeds have been found to be injurious to other plants. According *to Copeland ("Rice," p. 27), Villegras attributes* to this cause the poor growth of rice preceded by cogon grass (lalang).

Onodera (Ber. Ōhara Inst landw. Forsch. 1923, 2, 383) showed that the gases from the decomposition of green manures may have a harmful effect on the growth. In laboratory experiments using "gingo" (*Astralaga sinicus*) as a green manure, the growth of rice was improved by applications of lime, or calcium carbonate, or by treatment of the soil with H_2O_2. *On the field scale the best results were* obtained by liming, the application of superphosphate and draining of the water in the middle of the growing season to allow the soil to crack and aerate. Tziurupa and Bezruchenko (N. Caucassian Grain Inst. Coll Sci Papers, 1933, 1, 89) proved that the failure of second year planting of rice in Kuban under conditions of constant flooding was due to the utilisation *of oxygen by sulphur bacteria inhibiting the* germination and subsequent development of the seedlings.

EFFECT OF FERTILISERS ON THE COMPOSITION OF THE RICE CROP—Seven years' trials in Mandalay, Burma (Charlton, private communication), testing the effect of various fertilisers on the composition of the crop showed that farmyard manure and super phosphate were by far the most important in this direction. The percentage increase in "mineral" content above that of the control plots was as follows

	N	P_2O_5	K_2O
F Y M Grain .	3	14	14
„ Straw	8	160	17
Super. Grain .	10	14	8
„ Straw	6	167	−1
Am Sulp Grain	0	−16	−8
„ „ Straw	0	−20	−7
Sod Nit. Grain	3	−6	−3
„ „ Straw	−5	−11	−1

Superphosphate was shown to be much more active than bone meal. Nitrogen manures used alone tended to reduce the P_2O_5 and K_2O in grain and straw. The effect being more pronounced with ammonium sulphate than with sodium nitrate, but this effect was not shown when super was given in addition. Potash had very little effect on the composition of the grain, dung, in fact, being the only manure that affected the potash content to any appreciable extent. Apart from an 8% increase in P_2O_5 in the grain the effect of lime was negligible.

ANALYTICAL—Only a few methods of special *interest will be mentioned.*

Rice Flour, and Starch—Wagenaar (Z. Unters Lebensm 1927, 54, 357; 1928, 56, 205) describes *microscopical methods for the detection and* determination of rice flour in other flours and in spices. One method depends upon the adsorption of an acid dye, fuchsin-S, by the protein granules. The peculiar distribution of these in the rice grain gives a characteristic appearance to the particles of rice flour. This method is not applicable to the examination of *pepper, but a solution of carmine in ammonia* and glycerin is quite satisfactory.

Tuffi and Borghetti (Annali Chim Appl. 1935, 25, 331) give the following *method for the* detection of rice starch in wheat flour. A mixture of 10 g. of the flour with 300 c.c. of H_2O is left for 5 minutes, the supernatant, milky liquid being decanted and left for 5 minutes; a third similar settling is carried out. A drop of the resulting liquid, spread on a microscope slide, is allowed to dry, and the residue fixed by treatment for 5 minutes with methyl alcohol. The dry residue is stained for 5 minutes with a fresh mixture, in equal volumes *of 0 2% methylene blue and 0 1% eosin*. A solutions. After washing with water the rice starch

granules appear bluish-green, large wheat starch granules colourless or pale blue, and the smaller ones colourless; masses of violet-stained protein are usually seen; 1% rice starch is detectable.

Rice in Linseed Cake.—Cecconi and Ferrari (Ann. Falsif. 1935, **28**, 335) describe a method for detecting rice in linseed cake based on the high percentage of ash in the crude fibre.

Determination of Starch in Rice and Other Cereal Products.—Hall (J.S.C.I. 1931, **50**, 429T) suggests that the term starch "be reserved to describe all matter included in and within the geometrical envelope of the starch grain irrespective of its chemical and physical constitution." The malt-diastase methods of O'Sullivan (J.C.S. 1884, **45**, 1), slightly modified, Brown and Millar (Trans. of the Guinness Res. Lab. 1903, **1**, 79), and Tempus (Naturprodukte, 1923, 52), when applied to rice give figures which are in accordance with the starch determined by "difference" and with figures obtained in the commercial extraction of starch from rice, and therefore satisfy the authors' definition of starch.

Rice Husks in Bran.—Marchadier and Goujon (Ann. Falsif. 1924, **17**, 328) describe a method for determining rice husks in wheat bran. The method depends on the large proportion of silica present in the ash of the rice husk. Wheat bran yields an average of 5·5% of ash, and when this ash is treated with sulphuric and hydrofluoric acids, evaporated, and re-ignited, the loss or gain in weight does not exceed 0·2%. Rice husk yields 16·3–17·5% of ash, and the decrease in weight after treatment with H_2SO_4+HF is about 94% (15·1–16·4% calculated on the husk).

Raunier and Pau (Ann. Falsif. 1930, **23**, 229) state the amount of adulterant is determined by calculating the ratio of ash to silica, the figures obtained being for bran 7·78, sawdust 2·25, rice hulls 1·05. Rice hulls and sawdust give different colours from those given by bran and sharps when treated with iodine or with methyl-*p*-phenylene-diamine sulphate or with phloroglucinol and phosphoric acid. To characterise the adulterant, parallel colorimetric tests are made on the sample and on a mixture made according to the results calculated from ash and silica content.

According to Amos (Analyst, 1929, **54**, 332), rice husks may readily be detected under the microscope after boiling the sample with chloral hydrate, for the cells of the outer epidermis are arranged in longitudinal rows, are square in general outline, and have very sinuous side walls. Dagger-like hairs or hair scars are also to be seen. A normal bran has a fibre content of 7–10%, sharps 4·5–6·5%, but rice husks contain about 40% fibre. Honcamp and Pfaff (*l.c.*) estimate the husk in rice meal, etc., by heating with dilute HCl. The heavier sediment is washed, by decantation, free from dissolved and suspended matter, dried, and weighed.

Sand in Rice Flour.—Edilhauser (Chem.-Ztg. 1930, **54**, 44) incinerates 5 g. of the material over a micro-bunsen, boils the ash for 10 minutes with 10% HCl. The liquid is filtered and the filter paper with residue is gently boiled for ½ hour with 100 c.c. of 1·25% KOH. The residual sand is washed with very dilute HCl, ignited, and weighed.

Determination of "Silver Husk."—The determination of "silver skin" or "silver husk" in rice is a measure of the vitamin B content. Goudswaard (Pharm. Weekblad, 1933, **70**, 770; Pharm. Tijds. 1933, **10**, 112) enumerates the various methods for determining the vitamin B content of rice. He suggests a new method of double staining the grains, first in a medium (diluted 10 times) consisting of equal parts of 10% aq. $K_4Fe(CN)_6$ in acetic acid, then in $FeCl_3$, and finally in a medium of 5% $PhOH$ and 1% fuchsin in 10% $EtOH$ similarly diluted. The silver skin of the unpolished rice is stained red and the kernels with no silver skin (polished rice) are coloured deep blue.

WILD RICE (*Zizania aquatica*).—Winton (*l.c.* p. 155) quotes analyses of the grain from this species. "It is sometimes known as Indian, water, or black rice and water oats, grows in the wet marshes of streams and lakes both on the coast and inland." Johnson (U.S. Daily Consular and Trade Rep. 1912, **15**, 258) states that "in the province of Ontario, Canada, and neighbouring states of the U.S.A. the Indian tribes gather the crop in canoes, dry it in the sun, parch it in iron pots, and thrash out the kernels." Kennedy (J. Agric. Res. 1924, **27**, 219) describes it as an annual grass growing extensively in North America. By feeding experiments on rats it was found to be an inadequate food. Its proteins are of low biological value, its inorganic constituents are insufficient for growth, and it is deficient in vitamin A. It has, however, a greater food value than cultivated polished rice, since it contains more protein (14%), which is of better quality, and sufficient vitamin B.

COMPOSITION OF WILD RICE.

	Water %	Protein %	Fat %	N-free extract %	Starch %	Soluble carbohydrates %	Fibre %	Ash %
Woll:								
Parched . .	9·54	13·00	0·86	74·04	—	—	1·12	1·44
Sun-dried . .	9·99	13·65	0·88	72·68	—	—	1·22	1·58
Kennedy:								
I	7·74	13·36	0·46	75·96	65·26	2·98	1·39	1·09
II	7·85	13·97	0·89	74·50	61·69	3·69	1·41	1·38
III	8·93	14·62	0·72	72·62	60·47	2·33	1·94	1·17
IV	7·83	14·40	0·66	74·57	62·03	2·93	1·29	1·25

MINERAL CONSTITUENTS (KENNEDY).

K_2O %	Na_2O %	CaO %	MgO %	P_2O_5 %	SO_3 %
0 066	0 086	0 025	0·133	0 971	0 628

ACKNOWLEDGEMENTS.—Where reference to the original papers has not been possible, use has been made of the following. "British Chemical Abstracts"; Winton, "Structure and Composition of Foods," Vol 1, Copeland, "Rice"—to the authors of which thanks are due. W. R. S. L.

WHEAT.

Wheat has been cultivated for at least 6,000 years, and one of the earliest varieties, Emmer, is still found among isolated races For the origins of wheat, *see* Vasilov, "Study of Origins of Cultivated Plants," Inst Appl Botany, Leningrad, 1926, Elliot Smith, Nature, 1927, **119**, 81, Percival, *ibid* 157; Peake, *ibid.* 158; and Int Rev. Agric, Pt 2, 1929, **20**, 420 *Existing varieties are described* by Percival, "Wheat Plant," 1921, and are divided into three species, diploids, tetraploids and hexaploids, distinguished by chromosome numbers of 14, 28 and 42 respectively. The diploid *Triticum monococcum* (Einkorn) is a very ancient species, probably originating in Asia Minor, where it is still found wild and occasionally cultivated. The tetraploids, which probably originated in Abyssinia, include *T. dicoccum* (Emmer), *T. turgidum* (rivet wheat), native to the Mediterranean but still grown in England, and *T. durum*, the macaroni wheats The hexaploid wheats include the very important bread wheats, *T vulgare*, and the rarely cultivated *T Spelta* They appear to have been disseminated from Afghanistan and Upper India at a later date than Emmer and Einkorn.

Wheat is now the most widely used of all cereals, owing to high nutritive value combined with the dough forming properties of the gluten. While superior to rice and maize, especially in protein and mineral content, it is about equal in food value to barley, oats, and rye, but is unique in possessing the coherent gluten which makes it pre eminently suitable for bread making.

The composition of the wheat grain varies greatly with the variety and the climate and to a smaller extent with soil, fertilisation, and time of harvesting (Humphries and Biffen, J. Agric. Sci. 1907, **2**, 1, Biffen, *ibid.* 1909, **3**, 86; Jacob, Z. angew. Chem. 1935, **48**, 246, Bayfield, Ohio Agric. Exp. Sta Bull. No. 563, 1936). The greatest variation is in the cellulose content, the least in the fat (Berczeller and Wastl, Biochem. Z. 1927, **181**, 117). The changes in composition of the developing grain have been investigated by Teller (Ark. Exp. Sta. Bull. No. 52, 1899), Brenchley and Hall (J. Agric. Sci. 1909, **3**, 195), and Woodman and Engledow (*ibid.* 1924, **14**, 563). The most marked change is in dextrose content, which is relatively very high in the early stages of grain development. The immature grain is also richer in nitrogen and ash, and has a slightly higher diastatic activity than the ripe grain. The material entering the grain is of nearly constant composition throughout. About a quarter of the nitrogen is at first present in the form of soluble compounds; these are converted almost wholly into protein. In the last stages, the chief change is loss of water, finally so rapid that the weight of the grain falls. According to Neumann ("Brotgetreide u. Brot," 1929, 3rd ed, p 175), an average sample of wheat contains:

Water %	Protein %	Fat. %	Carbohydrate. %	Fibre. %	Ash. %
15 0	11 0	1 9	68 5	1 9	1 7

Other analyses are given by the authorities already quoted and by Aloj and Untersteiner (*Quad. Nutrizione*, 1936, **3**, 32). These constituents are by no means uniformly distributed through the grain: the protein, fat, fibre, and minerals are concentrated in the bran and germ, while the endosperm (about 85% of the grain) consists largely of carbohydrate, although the protein of the endosperm is actually considerable and is responsible for the bread-making properties.

Of the qualities which vary with variety, etc, the most important from the baker's point of view is protein (gluten) content. This is affected much more by climate than by any other factor, as is indicated by the following results of experiments by Leclerc and Leavett (U.S. Dept Agric. Div Chem. Bull. No. 128, 1910).

Year	Origin of seed	Protein in seed	Protein in product grown in Kansas	California	Texas
1906	Kansas	16 22	19 13	10 38	12 18
1907	Kansas	19 13	22 23	11 00	16 97
1907	California	10 38	22 23	11·33	18 22
1907	Texas	12·18	22 81	11·37	18 21

The English or North western European climate tends to produce soft, starchy wheats of low protein content, an average figure being 7 to 8%. High protein wheats, of an average content of 12–14%, are grown in the prairie regions of North America. Wheats of intermediate protein content and baking quality are grown in other certain well-defined areas. Although wheat is stated to be grown in every country in the world except Siam there are, in fact, eight great and distinct wheat regions in the world.

A *Europe:*
  (1) The plains of Southern Russia and the Danube Basin, the latter including Rumania and Hungary.
  (2) The countries bordering the Mediterranean Sea, especially Italy.
  (3) North-western Europe, *e g.* Germany, France, Holland, Belgium, Great Britain.

B North America:
  (1) The great central plains of Canada and U.S A. which are really one region although belonging to different countries
  (2) The Columbia Basin in the extreme north west of U.S.A., *i.e.* Eastern Washington and Oregon.

C. Northern India, mainly the Indo Gangetic Basin and Punjab.

D. Central Argentina.

E. Southern Australia.

"Strength" or good baking quality, however, is not necessarily always associated with high

protein content. Durum or macaroni wheats have a high protein content but are not of satisfactory baking quality. "Strength" is also associated with variety. Fife, for example, shows marked "strength" when grown in England although many foreign "strong" varieties become "weak" when grown in our climate.

Spring wheat usually contains more protein than winter wheat. This is not a case of cause and effect, but is due to spring sowing being general in those climates which produce high protein wheats. (For a further discussion, *see* Fisher and Jones, "The Wheats of Commerce," 2 vols., 104 pp., London, 1932.)

The proteins of wheat have been studied by many workers. Osborne (Amer. Chem. J. 1893, **15**, 392; 1894, **16**, 524; Amer. J. Phys. 1905, **13**, 35; 1906, **17**, 223; Carnegie Inst. Wash. 1907, Pub. 84) divides them into *gliadin* and *glutenin*, forming nearly all the protein of the endosperm, and *leucosin*, *globulin*, and a small quantity of one or more *proteoses*, contained chiefly in the embryo. Gliadin is insoluble in neutral aqueous solutions, but distinguished by ready solubility in neutral 70% alcohol. Glutenin is similar in elementary composition, soluble in very dilute acids and alkalis, but insoluble in dilute alcohol or neutral aqueous salt solutions; it differs from gliadin in the proportions of the decomposition products obtained on boiling with strong acids. Leucosin resembles albumin, is freely soluble in water, and coagulates on heating the solution to 50°–60°. The globulin is similar to that found in other seeds. The fractionation of wheat protein by means of various solvents has been investigated by Sharp and Herrington (Cereal Chem. 1927, **4**, 249). The gliadin : glutenin ratio was formerly thought to determine the baking quality of flour (Fleurent, Ann. Sci. agron. fr. 1898 (2), **4**, (i), 371), but recent investigations show no correlation (Kosmin and Popzowa, Mühlenlab. 1934, **4**, 153; Feyte, Ann. Agron. 1935, **5**, 72). Moreover, according to Blish (Cereal Chem. 1936, **13**, No. 5, suppl. 16), these fractions are themselves complex mixtures, varying in composition with the conditions of preparation, while Rich (*ibid.* 1936, **13**, 522) considers wheat protein to be a single individual. On hydrolysis, wheat protein yields an exceptionally large amount of glutaminic acids and of ammonia, about the same quantity of histidine as most seed proteins and relatively little arginine and lysine (Osborne, *l.c.*). The amino-acids essential for growth are present in larger proportion in the protein of the bran than in that of the endosperm (Murphy and Jones, J. Biol. Chem. 1926, **69**, 85).

The carbohydrate of wheat, especially of the endosperm, is mainly starch; dextrin, reducing sugar, and sucrose are also present, mainly in the germ. The germ also contains nearly all the fat.

The average mineral content of wheat is given in the following table, compiled from various sources:

	Fe %	Ca %	K %	Na %
Whole wheat	0·0050	0·045	0·473	0·039
Bran . .	0·0078	0·120	1·217	0·154
Germ . .	—	0·071	0·296	0·722

	P %	Cl %	S %	Mg %
Whole wheat	0·423	0·068	0·181	0·133
Bran . .	1·215	0·090	0·247	0·511
Germ . .	1·050	0·070	0·325	0·342

A small quantity of manganese is also an essential constituent; its variations have been investigated by Albizzati and Carradó (Ann. Soc. cient. Argent. 1936 (3), **121**, 97). The calcium : phosphorus ratio (1 : 10) indicates that wheat foods must be supplemented by others rich in calcium, the ratio considered necessary for health being 1 : 1. The phosphorus is present mainly as phytin (in which form very little can be assimilated), nucleotides, and lipins; in wheat germ the proportion of the total phosphorus present in these three forms of combination is 42, 28, and 9% respectively (Javillier and Colin, Bull. Soc. Chim. biol. 1933, **15**, 1552). The phosphatides of germinating wheat contain (saturated) palmitic and (unsaturated) linolic acids in the ratio of 1 : 5 (Diemair and Bleyer, Biochem. Z. 1935, **275**, 242).

Vitamins B_1, E, B_2, and carotene, which can act as a precursor of vitamin A, especially the first two, are present in wheat, chiefly in the germ and bran. Wheat germ is by far the richest known source of vitamin E.

The germ, constituting about 2½–3% of the grain, is generally removed in milling, on account of its adverse effect on the baking and keeping qualities of the flour, the fat present in large proportion tending to turn rancid. To enhance the keeping qualities of the separated germ, heat treatment is proposed (Hertwig, Cereal Chem. 1931, **8**, 226; Wanklyn and Stacey, B.P. 332847). Attempts to isolate the constituent responsible for spoiling the baking quality have so far been unsuccessful, though it is known to be soluble in water, not in fat solvents, and to decrease with ageing of the germ (Sullivan, Near, and Foley, Cereal Chem. 1936, **13**, 453; Geddes, Nat. Res. Coun. Ottawa Ann. Rpt. 1932, **15**, 84). According to analyses in Die Mühle, 1932, **69**, 1103, the composition of wheat germ is approximately:

Water. %	Protein. %	Fat. %	N-free extract. %	Fibre. %	Ash. %
11	32	9	42	1	5

Germ oil, d_{25} 0·9268, iodine number 125·6, contains linolenic, linolic, oleic, palmitic, stearic, and lignoceric acids (Jamieson and Baughman, Oil and Soap, 1932, **9**, 136); its absorption spectra have been studied by Bowden and Moore (Nature, 1933, **131**, 512; **132**, 204) and by Morton and Edisbury (*ibid.* **131**, 618).

Several pigments are present in wheat, the most important being carotene (pro-vitamin A). Bran contains a yellow indicator which it is suggested could be used for the determination of bran in flour (Schulerud, Mühlenlab. 1936, **6**, 129).

Wheat contains many enzymes—amylolytic, proteolytic, and oxidising. For bread-making, the amylases are of great importance, as they convert the starch into sugars which the yeast can utilise.

Methods of Analysis.—In the analysis of wheat and wheat flour, the ordinary methods employed for feeding stuffs are followed, the only special determinations required being those of gluten and gliadin.

For the determination of gluten 10 or 20 g. of dry flour, or of the ground wheat from which the husk has been sifted, are weighed out on to a beaker or porcelain dish, moistened with water, and kneaded up with a spatula into a dough. This is then transferred to a piece of bolting cloth about 8 ins. square, the silk is gathered together over the dough, and the dough is kneaded in several changes of water or under a tap until no more starchy liquid flows away, being finally squeezed in the air until it ceases to lose water. The gluten will then generally form an elastic coherent mass which can be removed from the silk without loss, weighed in its wet condition, spread on a tared sheet of glass or porcelain basin, dried at 100° to a constant weight, and weighed again. The ratio between wet and dry gluten is regarded as of some importance. For more accurate mechanical methods of gluten washing, *see* Halton and Fisher (Cereal Chem. 1936, 13, 575). For gliadin, 5 g. of flour are put in a flask with 250 c.c. of 70% alcohol, and shaken in a machine for 6 hours. The mixture is then rapidly filtered, and 100 c.c. of the solution are placed in a Kjeldahl flask. The alcohol is distilled off and the nitrogen in the residue is determined in the usual way. Nitrogen×5.68= gliadin.

For detailed methods of wheat and flour analysis, *see* "A.A.C.C. Cereal Laboratory Methods," 1935, "A.O.A.C. Official and Tentative Methods of Analysis," 1930.

The proportion of rye mixed with wheat flour can be determined by the percentage of the total protein soluble in a saturated solution of calcium sulphate (König and Bartschat, Z. Unters. Nahr. Genussm. 1923, 46, 321; Analyst, 1924, 49, 187).

For other tests relating to baking quality, *see* BREAD.

Wheat straw is of more variable composition than the grain, since the plant tends to keep the composition of the seed constant at the expense of other parts. By the time ripening is complete, nearly all the nutritionally valuable constituents are transferred to the grain; for use as fodder, therefore, straw cut early is preferable. Typical analyses of wheat straw are given in the following table, due to König:

Origin	No of samples	% Water.	% Fat.	% Protein.	% N free extract.	% Crude fibre	% Ash
English winter sown	—	13.6	1.3	3.3	39.4[1]	37.1	5.3
German winter sown	—	14.3	1.2	3.0	35.9	40.8	4.85
American spring sown	7	9.6	1.3	3.4	43.5	38.0	4.2

[1] Carbohydrates.

Analyses of the ash of mixed samples grown on different plots at Rothamsted over the ten years 1882–1891 gave the following results:

	%
Ash in dry matter	5.52–8.13
Ferric oxide	0.31–0.94
Lime	3.49–9.14
Magnesia	1.41–2.46
Potash	9.92–25.84
Soda	0.03–0.58
Phosphoric acid	2.26–4.26
Sulphuric acid	3.44–6.72
Chlorine	1.66–6.59
Carbonic acid	0.00–1.25
Silica	45.59–67.70
Sand and charcoal	1.41–3.78

In addition to supplying litter and fodder, wheat straw is used in building materials, for packing, for making matting and yellow wrapping-paper, and as a source of cellulose and of furfural for synthetic resins (Ray, Int. Rev. Agric. 1934, 25, 525T). E. A. F.

CEREBROSE, the sugar of the brain, first isolated from this organ by Thudichum, is in reality galactose. The cerebrosides *phrenosin*—also called *cerebron*—*kerasin*, and *nervon*, are found in nerve and brain tissue in considerable amounts. E. F. A.

CEREBROSIDES are galactolipins occurring in the brain in which a higher fatty acid is combined with galactose and sphyngosine, the higher amino alcohol

$$CH_3\cdot[CH_2]_{12}\cdot CH{:}CH\cdot CH(NH_2)CH(OH)CH_2\cdot OH$$

CERERITE *v.* CERIUM METALS AND EARTHS.

CERESIN, *Protoparaffin*, is obtained from "earth-wax," *i.e.* ozokerite. It occurs in commerce in the form of thin, round masses several inches in diameter, of a dazzling white appearance; inodorous, and transparent at the edges. It is harder than paraffin wax, does not sweat, and usually has a fine crystalline structure. It yields paraffins on distillation, but paraffins have not yet been converted into ceresins (Tokmanov, 1930, B, 596; Sachanov and Bestuschev, Petroleum, 1926, 22, 48). The melting point is between 75° and 80°. It is not attacked by acids, either in the cold or when heated; nor by alkalis, which do not saponify a trace of it. It is used as a substitutute for beeswax. The determination of ceresin in ozokerite can be effected by treating the benzine solution with *sulphosil* (silica gel activated with sulphuric acid), the ceresin remaining unadsorbed (Tokmanov, 1928, B, 592).

For the detection of paraffins in ceresin, *see* Holde and Schünemann (Z. angew. Chem 1928, 41, 368). On oxidation it yields a mixture of liquid and solid acids consisting chiefly of a mixture of polymerised unsaturated fatty acids, acid value 115, iodine value 11 (Marcusson, Chem.-Ztg. 1925, 49, 166).

CERFLUORITE. Mixed cubic crystals obtained by fusing calcium fluoride with cerium fluoride.

CERIN. The constituent of beeswax that is soluble in alcohol; it consists chiefly of cerotic acid. The term is also applied to the wax extracted by alcohol from cork.

CERINE *v.* CERIUM METALS AND EARTHS.

CERINSTEIN *v.* CERIUM METALS AND EARTHS.

CERITE. A hydrous silicate of cerium metals. Rammelsberg's analysis (1859) showed the presence of 64·55% Ce_2O_3 with 7·28% $(La,Di)_2O_3$ and approximated to the formula $2Ce_2O_3 \cdot 3SiO_2 \cdot 3H_2O$. Later analyses showed a predominance of lanthanum and didymium, suggesting the name lanthanocerite. Crystals are orthorhombic, but of rare occurrence. The mineral is usually found as reddish granular masses much resembling in appearance certain varieties of corundum, from which, however, it is readily distinguished by its lower hardness (H. 5½; sp.gr. 4·9). It occurs as a bed in gneiss at Bastnäs in Sweden, and was the material in which the element cerium was first detected. L. J. S.

CERIUM. Symbol Ce. At. no. 58. At. wt. 140·125 ±0·007; 2 isotopes 140 and 142. The most abundant of the rare-earth elements and estimated to be more plentiful terrestrially than silver, gold or platinum. The metal has been prepared by (1) the electrolysis of the fused chloride with or without an admixture of barium or calcium chloride or alkali chloride; (2) the electrolysis of a mixture of cerium dioxide and cerium fluoride (Borders and Stockem, D.R.P. 172529; Muthmann *et al.*, Annalen, 1902, **320**, 231; 1904, **331**, 1; 1907, **355**, 116). By the latter process, the yield corresponds with 57% of a current of 750 amperes and 7·5 volts with current densities of 9–10 amperes and 3 amperes per sq. cm. at cathode and anode respectively.

A cerium amalgam is readily obtained by electrolysis of anhydrous cerous chloride solution in methyl or ethyl alcohol using a mercury cathode which is agitated to prevent formation of crust. This amalgam, which may contain 3% of cerium, is enriched to 15% of this metal by vacuum distillation to 235°. Further heating to 1,000° in an oxide-lined crucible *in vacuo* furnishes metallic cerium (Jukkola, Audrieth, and B. S. Hopkins, J. Amer. Chem. Soc. 1934, **56**, 303). Electrolysis of fused cerous chloride using carbon anodes and molybdenum cathodes yields cerium of high purity (Trombe, Trans. Electrochem. Soc. 1934, **66**, 231).

Metallic cerium has the colour and lustre of iron; its hardness is comparable with that of silver or tin; m.p. 635° (Hirsch, Ind. Eng. Chem. 1911, **3**, 880), 623° (Muthmann and Weiss); sp.gr. of fused product of electrolysis 6·92 at 25°; specific heat 0·05112 (20°–100°); hardness (as determined by the scleroscope), 25·9 and 9·5 for rolled and freshly cut surfaces respectively; ultimate strength (as determined in an Olsen machine, with test bars of 0·212 in. diameter), 12,900 lb. per sq. in.; and no elongation with a constant load at 350 lb. Cerium is paramagnetic; magnetic susceptibility, $(K)+182{\cdot}2 \times 10^{-6}$ (Stefan Meyer, Monatsh. 1899, **20**, 369). In dry air the metal is moderately stable, but becomes superficially tarnished with yellow dioxide. The temperature of ignition in oxygen is about 150°–180° (Muthmann and Kraft, Annalen, 1903, **325**, 261). The metal is malleable and ductile; it has a fairly high latent heat of fusion and thermal conductivity. The heat of oxidation of the metal is 1,740 cals. per g.; the wire burns even more brightly than magnesium, and combines readily with the halogens. Cerium is very slightly attacked by cold water; a slow evolution of hydrogen occurs in boiling water, and the metal is tarnished black; it is readily dissolved by dilute acids, but concentrated nitric acid produces a brown deposit consisting mainly of dioxide. By heating the metal to 345° in hydrogen, cerium hydride is produced, without luminescence. At 1,000° it combines with nitrogen to form the nitride; and direct combination also occurs when the metal is heated in sulphur vapour (Hirsch, Chem. Met. Eng. 1911, **9**, 540). Cerium silicide ($CeSi_2$) is formed in crystals with steely lustre by the reduction of cerium oxide with graphite and silicon; it is stable in air but decomposed by acids (Sterba, Compt. rend. 1902, **135**, 170). The addition of cerium oxides to an electrolytic cell containing a melt of calcium fluoride, chloride, and silicate $CaSiO_3$, leads to a cathodic button of the silicide with some free silicon (Dodero, Compt. rend. 1934, **198**, 1593). This compound is brittle and when added to cerium in such proportion that the mixture contains about 15% of silicon, forms a good pyrophoric alloy. The magnesium-cerium alloys are excellent for thermal reduction processes since—the combination of the two metals being endothermic—more heat is developed by the oxidation of the alloy than by that of the two metals in admixture (Hirsch).

When scratched or rubbed with a steel edge cerium emits brilliant sparks, and this property has been utilised in the preparation of gas lighters. For a description of pyrophoric cerium alloys, *see* Eng. and Min. J. 1917, 212; Vogel, Z. anorg. Chem. 1917, **99**, 25.

Cerium alloys are produced by melting together the component metals under fused sodium-potassium chloride (Muthmann and Beck, Annalen. 1904, **331**, 46). Cerium-aluminium, $CeAl_4$, is thus obtained in rhombic or monoclinic needles with metallic lustre. The combination of these two metals is highly exothermic. Cerium and zinc combine with explosive violence, the alloy, containing 1 part of cerium to 2 of zinc, is blue. All such alloys rapidly become oxidised in the air.

Separation and Purification of Ceria (CeO_2).—Of all the rare earth oxides, ceria is most readily isolated in a pure state, and the following methods have been employed in separating this oxide from lanthana, praseodymia and neodymia.

(1) Treatment of the hydroxides suspended in aqueous caustic alkalis with chlorine; ceric hydroxide remains undissolved, while the other hydroxides are converted into soluble chlorides and hypochlorites (Mosander, 1842; Mengel, Z. anorg. Chem. 1898, **19**, 67).

(2) The mixed oxides dissolved in hot nitric acid and the solution evaporated down with ammonium nitrate until ceric ammonium nitrate

separates. The double salt is crystallised from nitric acid until the oxide left on ignition has a light-yellow colour (Auer von Welsbach, Monatsh. 1884, 5, 508; Schottländer, Ber. 1892, 25, 378); or the mixed oxides are treated with 4 times their weight of concentrated nitric acid and gradually heated to 60°. The solution, after decantation from any insoluble matter, is evaporated to a syrupy consistency, mixed with water from 10 to 30 times the weight of the oxides taken, and 1 g. of ammonium sulphate added for each litre of solution. The liquid is boiled for a few minutes, when a pale greenish-yellow precipitate of basic ceric nitrate and sulphate is formed, which is separated and washed with a solution of a mixture of ammonium nitrate and sulphate (Wyrouboff and Verneuil, Compt. rend. 1897, 124, 1230; Sterba, *ibid.* 1901, 133, 294).

(3) The solution of mixed nitrates is neutralised with ammonia and boiled with magnesium or sodium acetate and hydrogen peroxide whereby cerium is completely precipitated as a basic acetate (Meyer and Koss, Ber. 1902, 35, 672).

(4) The mixed ammonium double nitrates are boiled with aqueous ammonium persulphate, calcium carbonate being gradually added to keep the solution neutral. The precipitate contains all the cerium as ceric nitrate and sulphate mixed with calcium sulphate (Witt and Theel, Ber. 1900, 33, 1315; *cf.* Meyer and Marckwald, *ibid.* 3003).

(5) Electrolytic oxidation of cerous salts in supersaturated solutions leads to precipitation of purified basic ceric salts (U.S.P. 1707450). With cerous sulphate this oxidation is effected with 99% efficiency in the anodic compartment of a cell fitted with lead electrodes.

(6) The thermal decomposition of rare earth sulphates has been studied systematically and the dissociation pressures of the anhydrous sulphates determined at definite temperatures. By maintaining an appropriate partial pressure of sulphur trioxide above a heated mixture of isomorphous sulphates these were decomposed fractionally. Cerous sulphate on ignition readily yielded ceric oxide, whereas the associated rare earth metals remained as sulphates (H. H. Willard and R. D. Fowler, J. Amer. Chem. Soc. 1932, 54, 496).

(7) The joint action of potassium permanganate and a basic substance (mercuric oxide, zinc oxide, magnesia, sodium carbonate, etc.) on the rare earth oxides in neutral solution yields a precipitate containing all the cerium as ceric hydroxide (Stolba, 1878; Drossbach, 1896; D.R.P. 143106; Meyer, Z. anorg. Chem. 1903, 37, 378).

The last of the foregoing methods is generally applicable to the mixed oxides of the rare earths, and permits of the complete separation of cerium in one operation. These processes require to be repeated before the cerium is completely freed from the last traces of lanthanum; thorium also is difficult to remove completely. The solution of nitrates is mixed with an excess of ammonium carbonate, and treated with ammonia when the greater portion of the thorium is precipitated. To remove the remainder the cerium present is converted into the anhydrous sulphate and added to ice-cold water, when the pure hydrated salt separates (Wyrouboff and Verneuil, *l.c.*; Urbain, Ann. Chim. Phys. 1900, [7], 19, 184; Sterba, *ibid.* 1904, [8], 2, 193; Brauner, Z. anorg. Chem. 1903, 34, 103; Meyer, *ibid.* 37, 378; Orloff, Chem.-Ztg. 1906, 30, 733; 1907, 31, 562; Neish, J. Amer. Chem. Soc. 1909, 31, 517).

Only a small proportion of the cerium oxide extracted from monazite is used in the mantle industry, the greater amount is employed in the manufacture of sparking alloys for cigar lighters, etc. A further quantity is used (in the form of fluoride) for impregnating arc light carbons; in weighting silk, in the dyeing and photographic industries, and to a slight extent in medicine.

Cerium forms several series of compounds derived from the oxides **Ce_2O_3**, **Ce_4O_7(?)**, **CeO_2**, and **CeO_3**.

Cerous Compounds.

Cerium hydride, CeH_3(?) Cerium combines readily with hydrogen at 250°–270°, yielding a brownish-black amorphous hydride which not improbably consists to some extent of **CeH_4**. This product is stable in dry air at the ordinary temperature, but on heating it is converted explosively into cerium oxide and nitride (Matignon, Compt. rend. 1900, 131, 891; Muthmann and Kraft, Annalen, 1903, 325, 281).

Cerous fluoride, $2CeF_3,H_2O$ (John, 1874), known also in the anhydrous condition, and employed in the electrolytic production of the metal (*v. supra*; and *cf.* Brauner, 1881–1882).

Cerous chloride,

$$CeCl_3,7H_2O \text{ or } 2CeCl_3,15H_2O,$$

(Dennis and Magee, J. Amer. Chem. Soc. 1894, 16, 649; Meyer and Koos, Ber. 1902, 35, 2622).

The anhydrous chloride, a fusible deliquescent crystalline mass, is obtained by the following methods:

(1) Heating the dry oxalate or cerium dioxide in hydrogen chloride (Robinson, Proc. Roy. Soc. 1884, 37, 150).

(2) Decomposing cerium carbide with chlorine or hydrogen chloride.

(3) Reducing anhydrous cerous sulphate to sulphide by heating in hydrogen sulphide and decomposing the latter with hydrogen chloride (Muthmann and Stützel, Ber. 1899, 32, 3413). Cerous sulphide and hydrogen bromide yield cerous bromide.

(4) The anhydrous sulphate, when heated in a current of chlorine and sulphur chloride vapour, is converted directly into cerous chloride.

The dry chloride is readily soluble in alcohol, and ebullioscopic determinations of the molecular weight in this solvent gave numbers corresponding with **$CeCl_3$** (Muthmann, Ber. 1898, 31, 1829).

It forms double salts with the chlorides of mercury, gold, and platinum, and of certain organic bases.

Cerous bromide, $CeBr_3$, and ***iodide*, CeI_3**, are also known, as are the *bromate*,

$$Ce(BrO_3)_3,9H_2O,$$

and *iodate*, **$Ce(IO_3)_3,2H_2O$**.

Cerous hydroxide, $Ce(OH)_3$, a white precipitate obtained from soluble cerous salts with ammonia or caustic soda, is stable only in absence of oxygen. Exposed to air it becomes slowly oxidised to yellow ceric hydroxide, passing through an intermediate reddish-violet stage $xCe(OH)_3 \cdot yCe(OH)_4$ (Dennis and Magee, J. Amer. Chem. Soc. 1894, **16**, 649).

Cerous oxide has not been isolated with certainty, since the ignition of decomposable cerous salts (nitrate, sulphate, oxalate, etc.) leads to the production of cerium dioxide. The reduction of the latter oxide with hydrogen at high temperatures gives rise to an unstable dark blue oxide approximating in composition to Ce_4O_7.

Cerous sulphide, Ce_2S_3, a cinnabar-red solid devoid of definite crystal structure, is prepared by passing hydrogen sulphide over ceric oxide in a graphite boat at 1,000°–1,200°, then heated further to 1,550°–1,600°. It sinters at 2,000° and melts at 2,200° with volatilisation and slight decomposition which in a stream of hydrogen is slow even at 2,400°. It is unattacked up to 1,000° by nitrogen, carbon monoxide, magnesium, sodium chloride or cyanide, or by the sulphides of lead, antimony, or bismuth (Picon, Compt. rend. 1931, **192**, 684). It is moderately stable in air and only slowly decomposed by water or hydrogen chloride below 300°.

Cerium nitride, CeN, obtained by heating cerium in nitrogen (Muthmann and Kraft, Annalen, 1903, **325**, 261), or by passing ammonia over heated cerium carbide (Matignon, Compt. rend. 1900, **131**, 865), is decomposed by water, yielding cerium dioxide, ammonia, and hydrogen. An explosive *cerium azide* is precipitated by adding sodium azide to aqueous cerous nitrate (Curtius and Darapsky, J. pr. Chem. 1900, [ii], **61**, 408).

Cerous nitrate, $Ce(NO_3)_3,6H_2O$, prepared by (1) dissolving cerium dioxide in nitric acid in the presence of a reducing agent ; (2) decomposing cerous oxalate with strong nitric acid. Deliquescent triclinic crystals. When heated strongly, pure cerous nitrate leaves a residue of pale yellow cerium dioxide, but when praseodymium nitrate is present, the residual oxide is brown (Neish, J. Amer. Chem. Soc. 1909, **31**, 517).

Cerous sulphate, $Ce_2(SO_4)_3$. The anhydrous sulphate is produced by dehydrating the hydrated salt at 400°. Above 500° it decomposes, leaving a residue of dioxide. A saturated solution of the sulphate at 0° deposits the dodecahydrate, $Ce_2(SO_4)_3,12H_2O$ (asbestos-like needles). Above 3° this hydrate is labile, and at higher temperatures the solution of the sulphate deposits hydrates containing 12, 9, 8, 5, and 4 molecular proportions of water. With the sulphates of ammonium, sodium and potassium, cerous sulphate forms double sulphates isomorphous with the corresponding salts of lanthanum, neodymium and praseodymium. In moderately strong sulphuric acid, cerous sulphate gives rise to the acid sulphate, $Ce(HSO_4)_3$ (Brauner and Picek, Z. anorg. Chem. 1904, **38**, 322). This acid salt has been recommended as an oxidising catalyst in the production of *aniline black*, 0·3 g. of cerous oxide in this form sufficing to develop the black from 6 kg. of aniline hydrochloride.

Cerous carbonate, $Ce_2(CO_3)_3,5H_2O$, prismatic crystals, precipitated from solutions of cerous salts by ammonium carbonate, forms soluble crystalline double carbonates with the alkali and ammonium carbonates.

Cerous cobalticyanide,

$$Ce_2[Co(CN)_6]_2,9H_2O.$$

The most soluble of the rare-earth cobalticyanides in 10% hydrochloric acid (1,000 parts of saturated solution contain 10·75 parts of the salt).

Cerous tungstate, $Ce_2(WO_4)_3$, has been shown to have a crystal structure corresponding to *scheelite*, $CaWO_4$ (Beintema, Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 1011).

Cerous oxalate, $Ce_2(C_2O_4)_3,10H_2O$, crystalline white precipitate (Power and Shedden, J.S.C.I. 1900, **19**, 636), has been used medicinally as a sedative in sickness, particularly that of pregnancy, also in chronic diarrhœa, hysteria, epilepsy and migraine.

Cerous phenoxide has been recommended as a non-irritant disinfectant (J.S.C.I. 1909, 28, 1221 ; D.R.P. 214782).

Cerous acetylacetonate,

$$Ce(CH_3 \cdot CO \cdot CH \cdot CO \cdot CH_3)_3,3H_2O,$$

obtained by the interaction of cerous ammonium nitrate, acetylacetone, and ammonia (Urbain, Ann. Chim. Phys. 1900, [7], **19**, 184 ; Biltz, Annalen, 1904, **331**, 334).

Cerous dimethyl phosphate,

$$Ce_2(Me_2PO_4)_6,H_2O,$$

white, hexagonal plates, solubility of the anhydrous salt is 79·6 at 25°, and about 65 at 95° (Morgan and James, J. Amer. Chem. Soc. 1914, 36, 10).

For other cerous salts of organic acids, *v.* Biltz, Annalen, 1904, **331**, 334 ; Wolff, Z. anorg. Chem. 1905, **45**, 89 ; Morgan and Cahen, Chem. Soc. Trans. 1907, **91**, 477 ; Pharm. J. 1907, **78**, 428 ; Rimbach and Kilian, Annalen, 1909, **368**, 110 ; Pratt and James, J. Amer. Chem. Soc. 1911, **33**, 1330 ; Katz and James, *ibid.* 1913, **35**, 872 ; Erdmann and Wirth, Annalen, 1908, **361**, 190 ; Rimbach and Schubert, Z. physikal. Chem. 1909, **67**, 183 ; Jantsch and Grünkraut, Z. anorg. Chem. 1913, **79**, 305.

For complex cerium salts, *v.* Wyrouboff and Verneuil, Ann. Chim. Phys. 1906, [viii], **9**, 289 ; Barbieri, Atti R. Accad. Lincei, 1908, [v], **17**, 1, 540.

Ceric Compounds.

Cerium carbide, CeC_2 ; microscopic crystals, sp.gr. 5·23, prepared by melting together in the electric furnace cerium dioxide (192 parts) and sugar carbon (48 parts), using a current of 300 amperes and 60 volts (Moissan, 1896–1897) :

$$2CeO_2+C=Ce_2O_3+CO$$
$$Ce_2O_3+9C=2CeC_3+3CO$$
$$CeC_3=CeC_2+C$$

When decomposed with water, the carbide yields 75·5% acetylene, 20·5% methane, and 4% ethylene.

Ceric oxide (*syn.* Cerium dioxide), CeO_2; a white or light yellow powder, sp gr. 6 405, also in isotropic crystals, sp.gr. 6 76–7 905 The amorphous oxide is prepared by (1) the oxidation *of the metal in oxygen*; (2) *the ignition of* cerous salts (nitrate, sulphate, carbonate, oxalate) or ceric compounds (hydroxide, nitrate, sulphate). The colour of ceric oxide is pure white when prepared at low temperatures, but becomes pale yellow with decrease in volume on ignition (Spencer) It darkens when heated, but becomes nearly colourless or at most pale yellow when cooled The colour of ordinary ceria is probably due to traces of praseodymium peroxide. The ignited oxide is insoluble in hydrochloric or nitric acid or in dilute sulphuric acid. The crystalline form, obtained by heating *the amorphous variety with sodium chloride*, borax, or potassium hydrogen sulphate, is quite unaffected by acids or alkalis The dioxide is reduced with difficulty by aluminium and magnesium, when the corresponding cerium alloys are produced For further references to cerium dioxide, *v* Compt rend 1895, 120, 663, 1897, 124, 618, 1233, 1300, 125, 950, 1901, 133, 221; Drossbach, Ber 1900, 33 3303, 3506, Sterba, Ann Chim. Phys 1904, [8], 2, 193, Z anorg Chem 1903, 34, 103, 207, 37, 378), Hofmann and Hoschell, Ber 1914, 47, 238, Tiede and Birnbrauer, Z anorg Chem 1914, 87, *160*, Bekk Ber *1913*, 46, *2574*, Reimer, J Amer Chem Soc 1915, 37, 1636)

Ceric hydroxide, $Ce(OH)_4$, a yellowish precipitate obtained from soluble ceric salts by *means of ammonia or the caustic alkalis Cerous* hydroxide is slowly oxidised to ceric hydroxide by atmospheric oxygen and more rapidly by mild oxidising agents

Although ceric hydroxide is more stable than the lower hydroxide, the ceric salts are less stable than the cerous compounds Ceric chloride itself has not been isolated, but its additive compounds, R_2CeCl_6, with the salts of organic bases (pyridine, quinoline, triethylamine, etc) are stable in alcoholic solution

Colloidal ceric hydroxide is obtained by dialysing an aqueous solution of ceric am*monium nitrate The hydrosol is readily coagu*lated and dries to a gummy mass, soluble in hot water (Biltz, Ber 1902, 35, 4431, 1904, 37, 1095).

Ceric sulphate, $Ce(SO_4)_2$ The anhydrous salt is produced by heating the dioxide with strong sulphuric acid With the diluted acid, oxygen is evolved, and the resulting solution deposits, on concentration, ceri-cerous hydrogen sulphate,

$$2Ce(SO_4)_2.Ce_2(SO_4)_3.H_2SO_4.24H_2O$$

(Brauner, Z. anorg. Chem 1904, 39, 261), and *then yellow hydrated ceric sulphate,*

$$Ce(SO_4)_2.4H_2O$$

The former of these compounds corresponds with the intermediate oxide,

$$Ce_4O_7(=2CeO_2.Ce_2O_3)$$

Ceric sulphate is a useful oxidising agent in volumetric analysis, it is more stable than permanganate, and more reactive in presence *of acids and particularly fairly concentrated* hydrochloric acid. Its solution in dilute sulphuric acid is readily standardised potentiometrically against ferrous sulphate or sodium oxalate (Furman, J Amer. Chem Soc. 1928, 50, 755, 1675) Estimations with ceric sulphate can be effected in hot solutions or at lower temperatures with iodine chloride as catalyst In these cases methylene blue is a useful internal indicator. Thallium can be determined electrochemically in warm hydrochloric acid; tellurous acid may be estimated using chromic sulphate as catalyst (Willard and Young, *ibid.* 1928, 50, *1322 et seq*) Certain organic acids (tartaric, citric, malonic, malic, and glycollic) are oxidised by ceric sulphate but not formic, acetic, succinic, fumaric and maleic acids

Ceric sulphate forms a series of double sulphates (*e g* $Ce(SO_4)_2,2K_2SO_4,2H_2O$) with the alkali sulphates

Basic ceric sulphates, $4CeO_2.3SO_3.12H_2O$, and $2CeO_2.3SO_3.4H_2O$, have been described by Hauser and Wirth (Z anal Chem 1908, 47, 389), and $CeO_2.SO_3.2H_2O$ and $3CeO_2.4SO_3$ by J F Spencer (J C S. 1915, 107, 1265)

Ceric selenate, $Ce(SeO_4)_2$, a yellow compound obtained by the action of 50% aqueous selenic acid on ceric hydroxide (Meyer and Schultz, Z anorg Chem 1931, 195, 127)

Ceric nitrate, $Ce(NO_3)_3OH,3H_2O$ This basic salt separates from a solution of ceric hydroxide in nitric acid The normal ceric nitrate has not been isolated, but the double nitrates $R_2^ICe(NO_3)_6$, where R is ammonium *or an alkali metal, are well defined crystalline* substances, having a bright red colour, they are very hygroscopic and readily soluble in alcohol or water The double nitrates,

$$R^{II}Ce(NO_3)_6.8H_2O,$$

where R=Mg,Zn,Ni,Co,Mn, form a well defined series. These cerium double nitrates *are analogous to the corresponding* double nitrates of thorium

For other ceric salts, *v*. Barbieri, Atti R. Accad Lincei, 1907, [v], 16, 644; Ber. 1910, 43, 2214 For double ceric fluorides, *v*. Brauner, *Ber. 1881, 1914; Monatsh. 1882, 3, 1; Chem* Soc Trans 1882, 41, 68; Rimbach and Kilian, Annalen, 1909, 368, 101; Pozzi-Escot, Compt rend 1913, 156, 1074; Browning and Flora, Amer. J Sci. 1903, [iv], 15, 177)

For ceric acetylacetonate, $Ce(CHAc_2)_4$, *see* Job and Goissedet, Compt. rend. 1913, 157, 50

Cerium peroxide and its derivatives. The *addition of ammonia and hydrogen peroxide to* a solution of a cerous salt determines the precipitation of reddish-brown *hydrated cerium peroxide*, $Ce(O_2H)(OH)_3$. When cerous nitrate or chloride is added to concentrated aqueous potassium carbonate, the solution takes up atmospheric oxygen and assumes a deep red colour. The liquid slowly deposits crystalline dark red *potassium per ceric carbonate,*

$$4K_2CO_3.Ce_2(CO_3)_3O_3.12H_2O.$$

In the presence of glucose, this alkaline solution acts catalytically. When shaken in the air, oxygen is taken up and the per-ceric compound

produced. On standing, this substance is reduced by the glucose to cerous salt, and the colour disappears. Repeated shaking leads to renewed production of per-ceric compound, so that oxidation and reduction proceed alternately to an indefinite extent (Pissarjewski, J. Russ. Phys. Chem. Soc. 1900, **32**, 609; Z. anorg. Chem. 1902, **31**, 359; Wyrouboff and Verneuil, Compt. rend. 1898, **127**, 863; Job, *ibid.* 1898, **126**, 246; 1899, **128**, 178, 1089; 1902, **134**, 1052; 1903, **136**, 45; Engler, Z. anorg. Chem. 1902, **29**, 1; Ber. 1903, **36**, 2642; 1904, **37**, 49, 3268).

Applications of Cerium.—Metallic cerium (in the form of "mischmetal," *v.* CERIUM METALS AND EARTHS), has been used in the reduction of the refractory oxides of niobium (columbium), tantalum, molybdenum, etc.

The oxidising action of cerium compounds has led to their use in photography (Lumière, Compt. rend. 1893, **116**, 574), and as oxidising catalysts in organic preparations (Barbieri and Volpino, Atti R. Accad. Lincei, 1907, [v], **16**, i, 399), and as an ingredient of "driers." The oxides have been suggested for use in colouring glass (Chem. Ind. 1904, 27); in conjunction with manganese dioxide cerium compounds act in an opposite sense and decolorise glass (Löffler, Glashütte, 1936, **66**, No. 4, 63 1936). Cerium salts have been employed as mordants in dyeing. Hide powder decomposes cerium salts, fixing the element in the form of hydrated oxide. In the preparation of leather the hide partially reduces ceric sulphate or ceric ammonium nitrate, absorbing oxygen and yielding a good quality of leather which has a yellow tint and resists the action of water (Garelli, *Atti R. Accad. Lincei, 1907, [v], 16, i, 532).*

In addition to cerous oxalate, other salts (*e.g.* hypophosphate, and double ammonium citrate, tartrate, and lactate) have been utilised medicinally in the treatment of sea-sickness and nervous disorders. Incandescent gas mantles contain about 1% of ceria and 99% of thoria (Meyer and Anschütz, Ber. 1907, **40**, 2639).

(For the detection and estimation of cerium, *v.* CHEMICAL ANALYSIS.)

For a bibliography of cerium *see* Hirsch, J.S.C.I. 1912, 477. G. T. M.

CERIUM METALS AND EARTHS.

The Rare Earths. The so-called rare earths include a series of basic oxides, very similar in physical and chemical properties, which are generally found associated in certain comparatively rare minerals of complex composition (silicates, phosphates, titanates, columbates, tantalates, zirconates).

It should be realised that taking the series as a whole the rare earth metals are as plentiful in nature as cobalt, lead or zinc. Those of even atomic number are always more abundant than their allies of odd atomic number. Certain of the latter are extremely rare. This difference between the odd and even series suggests that their stability is intimately related to their sub-atomic structures.

The metals contained in these oxides may be divided roughly into two groups, named after the minerals *cerite* and *ytterbite*, in which the rare earths were first discovered.

The cerite metals (*cerium group*) are *lanthanum cerium, praseodymiun neodymium, illinium, samarium,* and *europium.*

The ytterbite metals (*yttrium group*, also referred to as the *lutecium group*) include, *gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium,* and *lutecium* with *scandium* and *yttrium* as near allies. Three of these elements, *europium, gadolinium,* and *terbium* form an intermediate series (the *terbium group*) connecting the cerium metals with the remaining rare-earth metals of the yttrium group proper. Closely associated with these elements is the metal *thorium. Zirconium* and *hafnium* are sometimes included in the category of the metals of the rare earths, but differ from the elements of the cerium and yttrium groups in having definitely amphoteric oxides.

HISTORICAL SUMMARY.—In 1794 ytterbite, obtained from Ytterby near Stockholm, was shown by Gadolin, its discoverer, to contain a new oxide, to which Ekeberg subsequently gave the name *yttria.* From the Swedish mineral cerite, Klaproth, in 1803 (Sitz. Akad. Berl. 1804, 155), isolated another new oxide which was called *ceria* by Berzelius and Hisinger (Ann. Chem. Pharm. 1804, **50**, 245), who also examined it. *Thoria* was isolated by Berzelius in 1828 from the silicate *thorite*, found at Brevig in Norway.

In 1839 Mosander isolated the oxides *lanthana* and *didymia* (Annalen, 1839, **32**, 235; 1842, **44**, 125) from cerite, and also effected a further separation from ytterbite of the earths *erbia* and *terbia* (Phil. Mag. 1843, **23**, 251; J. pr. Chem. 1843, **30**, 288). In 1878 Marignac separated from crude erbia a less basic colourless component which he called *ytterbia* (Compt. rend. 1878, **87**, 578), and this fractionation was speedily followed by Nilson's discovery of *scandia*, the least basic of the ytterbite earths, and its identification as the oxide of the hypothetical *ekaboron*, predicted by Mendeléeff. In the same year Cleve effected a further separation of the old "erbia" and found two new earths, namely *thulia* and *holmia* (Compt. rend. 1879, **89**, 478, 708). The doubt expressed by Marignac as to the homogeneity of didymia was shared by Delafontaine, on the ground of spectroscopic evidence (Compt. rend. 1878, **87**, 634), and substantiated by Lecoq de Boisbaudran (Compt. rend. 1879, **88**, 323), who isolated from this earth the less basic oxide *samaria.* The didymia left after the removal of the last-mentioned oxide was still regarded as a mixture by Brauner (Monatsh. 1882, **3**, 486; J.S.C. 1882, **43**, 278), and in 1885 Auer von Welsbach, by fractional crystallisation of the double didymium nitrates of ammonium and potassium, succeeded in separating this earth into two components, which he named *neodymia* and *praseodymia* (Monatsh. 1885, **6**, 477). Lecoq de Boisbaudran now showed that Cleve's *holmia* was a mixture containing a new constituent *dysprosia* (Compt. rend. 1886, **102**, 1003), the simple nature of which was afterwards confirmed by Urbain (*ibid.* 1904, **139**, 736; 1905, **141**, 521).

Gadolinia, which had been recognised by Marignac in *samarskite* (*ibid.* 1880, **90**, 899),

was isolated in a more definite form by Lecoq de Boisbaudran (*ibid.* 1889, 108, 165; 1890, 111, 409, 472), and by Bettendorf (Annalen, 1890, 256, 159; 1891, 263, 164; 1892, 270, 376), and further purified by Demarçay and by Urbain and Lacombe. Further researches by Demarçay on Cleve's samaria led to the isolation of *europia* (Compt. rend. 1896, 122, 728), an earth provisionally symbolised as Σ and afterwards shown to be identical with oxides indicated by the symbols Z_ϵ and Z_ζ (Lecoq de Boisbaudran, *ibid.* 1892, 114, 575; 1893, 116, 611, 674) and $S\delta$ (Crookes, *ibid.* 1885, 100, 1380, 1495; Proc. Roy. Soc. 1885, 38, 414).

Terbia, which occurs only in small amount in ytterbite, has been isolated in a purified state by Urbain, and Marignac's ytterbia (*l.c.*) has been fractionated by Auer von Welsbach (Monatsh. 1906, 27, 935), and separated into two components, *neoytterbia* and *lutecia*, by Urbain (Compt. rend. 1907, 145, 759), the former name has since been shortened to *ytterbia*

OCCURRENCE (v. "Das Vorkommen der seltenen Erden," Schilling, 1904; Phipson, Chem News, 1896, 73, 145). The following is a short description of the most important sources of the rare earths:

(For details concerning the various minerals, *see* under their respective headings.)

(1) *Minerals containing chiefly Cerium Earths.*

Cerite (*q.v.*) (also known as ochroite, cererite, cerinstein.

Orthite (allanite, bodenite, cerine, muromontite, pyrorthite, tautolite, uralorthite, wasite), a double silicate of aluminium and the cerium metals (16–25%), together with smaller quantities of thorium, iron, calcium, and the yttrium metals; found in Greenland, Scandinavia (Arendal, Hitterбe, Stockholm), United States (New York, North Carolina, Pennsylvania, Virginia, Texas), Ural Mountains (Miask), and in several localities in Germany.

Monazite (cryptolite, edwarsite, eremite, mengite, turnerite), an orthophosphate of the cerium metals $(Ce, La, Nd, Pr)^{III}PO_4$, containing 40–70% of these elements together with varying amounts of thorium (0–18%); it occurs in the plutonic and older volcanic rocks, and in the alluvial sands of the rivers and coasts of Brazil, North and South Carolina, and Travancore, in the Federated Malay States, Ceylon and Nigeria, etc.

Æschynite.—A complex columbate-titanate, containing approximately equal proportions (13–23%) of thorium and the cerium metals, together with a small proportion of the yttrium group, found at Hitterö (Norway) and Miask (Ural Mountains).

(2) *Minerals containing chiefly Yttrium Earths.*

Ytterbite (gadolinite), a basic silicate containing yttrium earths (40–48%) and cerium earths (5–10%), together with glucinum (beryllium) and iron; found in Colorado, Germany (Harz Mountains and Silesia), Scandinavia (Fahlun, Hittero, Ytterby), and Texas.

Yttrialite, a silicate of the yttrium metals (43–47%), thorium (10–12%), and cerium metals (5–8%), found in Texas.

Xenotime, a phosphate of the yttrium metals (54–64%), corresponding with monazite; it contains also smaller amounts of the cerium metals and thorium; found in Brazil, North Carolina, Georgia, Norway, Sweden, and Switzerland.

The following minerals contain the yttrium earths and smaller quantities of thoria and the cerium earths united with varying proportions of the more acidic oxides of columbium (niobium), tantalum, titanium, tungsten, tin, uranium, silicon, zirconium, and hafnium.

Fergusonite (bragite, kochelite), found in Ceylon, Greenland, Arendal, Ytterby, Massachusetts, North Carolina, and Texas

Yttrotantalite, found in Norway, Sweden, and the Ural Mountains.

Samarskite (nohlite, vietinghofite, ytteroilmenite), found in Canada, Connecticut, North Carolina, and Ural Mountains (Miask)

Polycrase, found in Canada, Scandinavia, and North and South Carolina.

Euxenite (loranskite), found in North Carolina, Norway (Hitteroe, Brevig), and Swaziland

Many other rare complex minerals (fluorides, zircono-silicates, titanates, columbates (niobates), tantalates, uranates, etc) contain considerable amounts of the rare earths, which are also not infrequently found in small quantities in commoner minerals (*e g.* limestones, apatites, scheelites, etc) Traces of the rare earth metals have been detected in mineral waters, in the ashes of plants, in urine, and in bone ash.

Extraction of the Rare Earths—The finely powdered mineral, made into a paste with concentrated sulphuric acid, is heated until the mass becomes dry and hard. The product is extracted with water, the solution treated with hydrogen sulphide to remove copper, bismuth, molybdenum, etc., and the metals of the rare earths precipitated as oxalates by the addition of oxalic acid The oxalates are decomposed at 400°, the residual oxides dissolved in dilute sulphuric acid, and the solution saturated with sodium or potassium sulphate, when the double sulphates of the cerium metals are precipitated whilst those of the yttrium metals remain dissolved

The complex minerals containing niobium (columbium), tantalum, titanium, etc., may be decomposed by hydrofluoric acid, when the foregoing elements form soluble fluorides, whilst the fluorides of the rare earth metals are precipitated. Or these minerals may be broken up by heating with strong sulphuric acid or potassium hydrogen sulphate and the rare earths precipitated by ammonia from the solution of their sulphates. These hydrated oxides are freed from the co precipitated niobium (columbium), tantalum, and titanium hydroxides by prolonged boiling with nitric acid, when the latter hydroxides separate in an insoluble form. The rare earths are precipitated as oxalates from their solution in nitric acid, the oxalates ignited, and the resulting oxides subjected again to the nitric acid treatment until a complete separation is effected. Or the minerals may be heated in the vapour of sulphur monochloride, S_2Cl_2, or carbonyl chloride, $COCl_2$, when the chlorides of niobium (columbium),

tantalum, titanium, etc., are volatilised, and the rare earth metals are converted into non-volatile chlorides (Hicks, J. Amer. Chem. Soc. 1911, **33**, 1492; Barlot and Chauvenet, Compt. rend. 1913, **157**, 1153).

The methods of separating and purifying the rare earths, which are further described under the appropriate headings (*v.* CERIUM) may be divided into the following two classes:

(1) Separations based on differences of basicity.

(*a*) The fractional precipitation of the earths with bases of varying strengths: ammonia, caustic alkalis, magnesium hydroxide, organic bases.

(*b*) The fractional decomposition by heat of the solid nitrates and other salts.

(2) Separations based on differences of solubility.

Considerable ingenuity has been shown in separating the metals of the rare earths by taking advantage of the slight differences of solubility exhibited by their salts with acids of widely different types. The following series does not exhaust the list of the compounds which have been utilised in these intricate separations: sulphates, double sulphates, nitrates, double nitrates, chromates, bromates, formates, oxalates, succinates, ethyl-sulphates, acetylacetonates, dimethyl-phosphates, glycollates, and sulphanilates (*cf.* James, J. Amer. Chem. Soc. 1912, **34**, 757).

The progress of these separations is controlled by chemical and physical methods.

(1) The chemical control consists in determining the equivalent of any fraction either by a gravimetric analysis of its sulphate (Krüss, Z. anorg. Chem. 1893, **3**, 44; Wild, *ibid.* 1904, **38**, 191; Brill, *ibid.* 1908, **47**, 464; Jones, *ibid.* 1903, **36**, 92; Brauner and Pavlíček, J.C.S. 1902, **81**, 1243), or by a volumetric analysis of its oxalate (Feit and Przibylla, Z. anorg. Chem. 1905, **43**, 202).

(2) The physical methods consist in observing the magnetic susceptibility of the fractions and their spectroscopic characteristics. The rare earths differ considerably in magnetic susceptibility; and determinations of its amount are readily made by the magnetic balance of Curie and Chereveau (Urbain, Compt. rend. 1908, **146**, 406, 922; 1908, **147**, 1286; 1909, **149**, 37; 1910, **150**, **913**; 1911, **152**, 141; 1914, **159**, 323).

The most convenient spectroscopic controls are (i) the *absorption spectra*, exhibited by solutions of the salts of many rare earths (*e.g.* neodymium, praseodymium, samarium, terbium, erbium, thulium, dysprosium, and europium); (ii) the *arc spectra*, in which all the rare earths give characteristic lines both in the visible and ultra-violet regions of the spectrum. Carbon electrodes are employed, the lower one containing a hollow in which is placed the salt under examination. The arc spectra are photographed and the lines identified by comparison with the known wave-lengths in the photograph of an iron spectrum taken under similar conditions. The method is extremely sensitive, although not equally so for different elements (*v.* CHEMICAL ANALYSIS and Exner and Haschek, "Die Wellenlängen der Bogenspektra," 1904; and Hagenbach and Konen, "Atlas der Emissionspektren der meisten Elemente," 1905). Other emission spectra (the flame, spark, and cathode luminescence spectra) have been found to give useful indications in certain cases (Crookes, Phil. Trans. 1883, **174**, [3], 891; Proc. Roy. Soc. 1885, **38**, 414; 1886, **40**, 77, 236, 502; Chem. News, 1886, **54**, 39, 54, 63, 76, 155; **55**, 83, 95; **56**, 59, 62, 72, 81; J.C.S. 1889, **55**, 255; Proc. Roy. Soc. 1899, **65**, 237; Lecoq de Boisbaudran, Compt. rend. 1885, **100**, 1437; **101**, 552, 558; 1886, **102**, 153, 899, 1536; **103**, 113, 627; 1887, **105**, 258, 301, 343, 784; 1890, **110**, 24, 67; Bettendorf, Annalen, 1892, **270**, 376; Baur and Marc, Ber. 1901, **34**, 2460).

The magnetic susceptibilities of rare-earth metals with anomalous valencies throw some light on the electronic structure of the metallic ions. Advantage is taken of the large paramagnetism of the metals and their salts. S. Meyer made susceptibility determinations of quadrivalent cerium and praseodymium (Physikal. Z. 1925, **26**, 51, 749), and later observers have examined compounds of bivalent samarium, tervalent gadolinium, and both bi- and tervalent europium and ytterbium (Klemm *et al.*, Z. anorg. Chem. 1928, **176**, 181; 1929, **184**, 352; Selwood, J. Amer. Chem. Soc. 1933, **55**, 4869; 1934, **56**, 2392; Hughes and Pearce, *ibid.* 1933, **55**, 3277). These determinations indicate that the susceptibility of a quadrivalent rare earth metal ion approaches that of the ion of a tervalent metal ion with one *less* atomic number, whereas the susceptibility of a bivalent rare earth metal ion approaches that of a tervalent metal ion with an atomic number *greater* by one. These regularities indicate the movement of valency electrons in and out of the 4_4 orbital quantum group. These magnetic susceptibilities when accurately determined afford a very exact means of analysis since the magnetic susceptibilities of mixtures of rare earth compounds are additive.

PHYSICAL AND CHEMICAL PROPERTIES OF THE RARE EARTHS AND THEIR MORE IMPORTANT COMPOUNDS.

Hydrides.—The rare earth metals combine directly at 220°–270° with hydrogen to form brittle amorphous solids ranging in colour from bluish-black (Ce and La), indigo blue (Nd), to green (Pr), and readily dissociated at higher temperatures (Muthmann, Kraft and Beck, Annalen, 1902, **325**, 261; 1904, **331**, 581).

Oxides and Hydroxides.—The metals of the rare earths were formerly supposed to be diads (*cf.* Wyrouboff, Bull. Soc. chim. 1889, [iii], **2**, 745; 1899, [iii], **21**, 118; Compt. rend. 1899, **128**, 1573), but they are now regarded as mainly tervalent elements forming oxides of the type R_2O_3, although cerium, neodymium, praseodymium, and terbium are capable of yielding higher oxides. The more stable oxides of thorium and zirconium are of the form RO_2. Later researches have shown that samarium, europium, and ytterbium have definite derivatives in which they behave as bivalent elements. There is also less conclusive evidence that lower

valency compounds exist in the cases of lanthanum, gadolinium, thulium, and lutecium. The present view that the metals of the rare earths have a characteristic group valency of 3 is supported by the following facts:

(i) The isomorphism of bismuth nitrate and certain nitrates of the rare earth series (Bodman, Ber. 1898, 31, 1237).

(ii) The cryoscopic and ebullioscopic determination of the molecular weights of the chlorides and acetylacetonates (Ber. 1898, 31, 1829; Compt. rend. 1901, 133, 289; Annalen, 1904, 331, 334); these salts are thus found to have the general formula RX_3.

(iii) The electrical conductivity of the chlorides and sulphates in aqueous solution (Z physikal. Chem. 1899, 30, 193; Amer Chem J. 1898, 20, 606).

(iv) The specific heats of cerium, lanthanum, and didymium (Annalen, 1873, 168, 45; Ber. 1881, 2821; Bull Soc. chim 1882, [2], 38, 139).

The rare earth oxides vary considerably in basic power, lanthana, praseodymia, neodymia, and ceria, Ce_2O_3, being the strongest; whilst ytterbia, lutecia, scandia, and cerium dioxide are among the weakest bases of the series. In general, the oxides (R_2O_3) of the cerium metals are stronger bases than those of the yttrium group.

The order of decreasing basicity is that of increasing atomic number from lanthanum, at. no. 57, to lutecium, at no 71. Lanthanum hydroxide is the strongest tervalent base known, being 1,300 times more basic then yttrium hydroxide. If the latter metal of atomic number 39 is included in the rare earth sequence it would form an exception, for Hopkins (J. Chem Educ 1936, 13, 363) places it between illinium (at no 61) and samarium (at no 62), whereas Endres (Z anorg Chem 1932, 205, 321) places it between gadolinium (at no 64), and dysprosium (at no 66).

The hydroxides are thrown out of solution as gelatinous precipitates by ammonia, ammonium sulphide, and the caustic alkalis, even in the presence of ammonium salts, but this precipitation is prevented by citric or tartaric acid (except in the case of scandium). Unlike thorium and zirconium, the metals of the cerium, terbium, and yttrium groups are not precipitated as hydrated peroxides from neutral solutions by hydrogen peroxide, but their peroxides separate from alkaline solutions (Brauner, Ber. 1881, 14, 1944; Cleve, Bull. Soc. chim. 1885, [ii], 43, 53). These peroxides are very unstable, evolving oxygen at even the ordinary temperature; they are completely destroyed by acids (v. CERIUM; cf. Melikoff and Pissarjewski, Z. anorg. Chem. 1899, 21, 70).

Chlorides.—The chlorides of the rare earth metals are deliquescent salts readily soluble in water or alcohol, and crystallising from the former solvent with 6 or 7 molecular proportions of water. The anhydrous chlorides, which are fusible at red heat, but very slightly volatile, are obtained either by evaporating their solutions to dryness with ammonium chloride and heating the double salt thus formed, or by heating the corresponding oxides with carbon in a stream of chlorine, or preferably by heating the oxide or dry sulphate in a current of sulphur chloride or carbonyl chloride or carbon tetrachloride (Matignon and Bourion, Compt. rend 1901, 133, 289; 1902, 134, 657, 1308; 1904, 138, 631; 1905, 140, 1181. Muthmann and Stutzel, Ber. 1899, 32, 3413; Petterson, Z anorg. Chem 1893, 4, 1; Chauvenet, Compt rend. 1911, 152, 87).

A comprehensive series of chlorides, bromides, and iodides of the rare earth metals has been prepared by Jantsch and collaborators (1929–1932) who have determined the melting points of these halides. In the first half of the group, the chlorides have the highest melting points, whereas in the second half it is the iodides which are least fusible. This difference suggests a variation in the space lattices of the two sets of halides.

The chlorides of the rare earth metals combine additively with ammonia and organic bases (e g pyridine; cf Compt rend 1905, 140, 141; J. Amer Chem Soc. 1902, 24, 540; 1903, 25, 1128; Ber 1902, 35, 2622), and exhibit a great tendency to form double salts with the less electropositive metals. The platinichlorides of the cerium metals are isomorphous and crystallise in regular octahedra (Ber. 1876, 9, 1722, Annalen, 1878, 191, 331).

Fluorides.—The rare earth metals, including thorium, are precipitated completely as gelatinous fluorides by soluble fluorides and by hydrofluoric and fluosilicic acids, in this respect differing from zirconium, which forms a soluble double fluoride.

Nitrides.—The rare earth metals when heated combine directly with nitrogen to form nitrides of the type $M\vdots N$. They are brittle amorphous solids, decomposed by moist air or by water, forming ammonia and the corresponding hydroxide.

Nitrates.—The nitrates of the rare earths dissolve readily in water or alcohol, those of the cerium group crystallising with 6 molecular proportions of water, whilst the corresponding salts of the yttrium group contain 3–6 mols of water. The cerium metals readily furnish stable crystallisable double nitrates with the univalent and bivalent metals (ammonium, sodium, magnesium, etc).

With a view to facilitating the separation of these closely allied metals, Newton Friend has studied (1928–1935) the solubilities of the nitrates, double magnesium nitrates, and selenates of lanthanum, praseodymium, and neodymium.

Sulphates.—The rare earths dissolve in dilute sulphuric acid, and the solutions deposit hydrated sulphates containing frequently 4, 8, or 12 mols of water. The octahydrated sulphates of praseodymium, neodymium, yttrium, gadolinium, and ytterbium are isomorphous (monoclinic); but the cerous salt

$$Ce_2(SO_4)_3,8H_2O$$

is rhombic. With excess of acid, the normal sulphates of the rare earths are converted into acid sulphates of considerable stability (Bull. Soc. chim. 1889, [3], 2, 745; Compt rend. 1902, 134, 657; Z. anorg. Chem. 1901, 28, 322; J.C.S. 1902, 81, 1243; James

and Holden, J. Amer. Chem. Soc. 1913, **35**, 559).

The sulphates of the rare earths have the characteristic property of combining with the alkali sulphates; the double sulphates of the cerium group are only sparingly soluble in concentrated solutions of the alkali salts, whilst those of the yttrium group are readily soluble. The double sulphates of the terbium group occupy an intermediate position, being moderately soluble in solutions of alkali sulphates.

The variable valencies of the rare earth metals have proved very useful in rendering possible methods of separation between any one of the elements and its neighbours. The quadrivalency of cerium (*cf.*) has long been utilised in separating this metal from the other elements of its sub-group. More recently the bivalency of the rare earth metals has been utilised, for when the lower valency is effective the solubilities of the sulphates resemble those of strontium and barium (Jantsch, 1929). This observation has been utilised in separating europium from other rare earth metals by electrolytic reduction in presence of the sulphate ion (Yntema, 1930). A solution of the oxides of samarium, europium, and gadolinium in hydrochloric acid was added to dilute sulphuric acid and electrolysed in a divided cell with mercury cathode and platinum anode. Colourless europous sulphate, $EuSO_4$, separated at the cathode and showed only a trace of samarium, thus achieving one of the most difficult separations in inorganic chemistry. With less than 2% of Eu_2O_3, co-precipitation with the isomorphous strontium sulphate is helpful. The method gives good yields of europous sulphate of high purity. Similarly, ytterbium can be separated from yttrium, erbium, and thulium by electrolytic reduction to ytterbous sulphate, $YbSO_4,xH_2O$, a light green salt. The method also serves to separate ytterbium from lutecium (Pierce, 1934). The tendency to form these bivalent sulphates decreases in the order europium, ytterbium, and samarium. The ease with which europium is reduced to the bivalent condition forms the basis of a rapid procedure for the complete separation of this element from its allies. A solution of rare earth chlorides rich in europium (70%), the remainder being neodymium, samarium, and gadolinium, was reduced with amalgamated zinc and concentrated hydrochloric acid, the progress of reduction being ascertained by the fading out of the absorption band (λ5253) due to europium. Excess of hydrochloric acid was then added, when colourless europous chloride dihydrate, $EuCl_2,2H_2O$, separated in 90% yield (McCoy, J. Amer. Chem. Soc. 1937, **59**, 1131).

Carbides of the rare earth metals may be prepared by heating the oxides with carbon in the electric furnace. They have the general formula MC_2. They are brittle, crystalline solids, transparent in thin layers and of a yellow colour. They are decomposed by water, forming a mixture of acetylene, hydrogen, ethane, and ethylene, and the hydroxide of the metal $M(OH)_3$.

Carbonates. — Ammonium, sodium, and potassium carbonates precipitate the neutral or basic carbonates from solutions of the rare earths; but these precipitates are soluble in excess of the reagents, and from the solutions thus obtained, crystalline double carbonates are deposited on evaporation. The carbonates of the yttrium metals are generally more soluble than those of the cerium group in solutions of the alkali carbonates.

Oxalates.—The rare earth oxalates are precipitated by oxalic acid or soluble oxalates in neutral or acid solutions, and the sparing solubility of these compounds in acids is a characteristic property which serves to separate the rare earths from other metallic bases (Ber. 1898, **31**, 1718; 1899, **32**, 409).

The oxalates of the rare earths proper dissolve only slightly in ammonium oxalate, differing in this respect from the oxalates of thorium and zirconium, the latter being also soluble in free oxalic acid (Brauner, J.C.S. 1898, **73**, 951). Aqueous ammonium acetate dissolves the oxalates of the yttrium group (Bull. Soc. chim. 1896, [iii], **15**, 338).

Formates.—The formates of the cerium group are less soluble than those of the yttrium group. These salts have proved useful in separating the elements of the terbium group.

Acetates.—The acetates of the cerium group are very soluble and crystallise with difficulty; those of the yttrium group are less soluble. Boiling with sodium acetate precipitates zirconium and thorium from solutions of their soluble salts, but not the rare earths proper, excepting cerium from ceric salts (Ber. 1902, **35**, 672).

Acetylacetonates. — Acetylacetone furnishes well-crystallised salts with the rare earths, and the fractionation of these compounds from alcohol has served in the separation of the yttrium group (Urbain, Compt. rend. 1897, **124**, 618; Bull Soc. chim. 1897, [iii], **17**, 98; Ann. Chim. Phys. 1900, [vii], **19**, 184; Biltz, Annalen, 1904, **331**, 60; Z. anorg. Chem. 1904. **40**, 218; Hantzsch and Desch, Annalen, 1902, **323**, 26; Biltz, *ibid.* 1904, **331**, 334; James, J. Amer. Chem. Soc. 1911, **33**, 1332; Morgan and Moss, J.C.S. 1914, **105**, 189).

Dimethyl Phosphates.—A solution of the rare earths is made in dimethyl phosphoric acid, the temperature raised, and the precipitate collected; additional fractions are obtained by evaporating the mother liquor. In the case of a material containing gadolinium with just sufficient terbium to colour the oxide orange-brown, the gadolinium collects in the most soluble fraction, and the terbium in the least soluble. Lanthanum, cerium, praseodymium, and neodymium are left in the mother liquor. The samarium, europium, and gadolinium salts, which are much less soluble than these, but more soluble than those of terbium, dysprosium, and holmium, erbium, thulium, yttrium, and ytterbium, collect in the least soluble fractions (Morgan and James, J. Amer. Chem. Soc. 1914, 36, 10).

Catechol Derivatives.—On adding catechol and alkali successively to solutions of the rare earth salts amphoteric compounds of the general type $HOR(O{\cdot}C_6H_4{\cdot}OH)_2$ are deposited. These

dissolve in acetic acid to crystallisable acetates (I) and in ammonia or alkali hydroxides to form

$$C_6H_4{<}^{O}_{O}{>}R\,OAc;\quad \left[\left(C_6H_4{<}^{O}_{O}{>}\right)_3 R\right]M_3$$

I. II.

the complex salts (II), where R=La, Ce, Pr or Nd; and M=Na, K or NH_4. Of the latter substances the cerium derivative is noteworthy since it dissolves in concentrated ammonia to a violet solution which on boiling deposits crystals of an intense violet colour (Fernandes, Gazzetta, 1926, 56, 682).

The Metals of the Rare Earths.—The oxides of the rare earths are very refractory substances, which have not been reduced directly; the metals are generally set free from the anhydrous chlorides. This reduction may be effected with sodium or potassium, but is preferably carried out electrolytically. The dry chlorides, mixed with a small proportion of alkali chloride, or barium chloride, are electrolysed in a copper crucible, fitted with carbon electrodes, the electrolysis being carried out with a current of 30–40 amps. and 12–15 volts The mixed metal collects in a molten state round the cathode, which passes through the bottom of the crucible. The anode is movable, so that the resistance and therefore the temperature can be increased until all the separated metal melts together A yield of 750 g of metal can be obtained with a current of 120 amps in 6 hours

Electrolysis of the chlorides in alcoholic solution with a mercury cathode leads to an amalgam of the rare earth element which when heated to 1,000° leaves a residue of the metal Amalgams having the general formula RHg_4 have been isolated where R=La, Ce, Pr or Nd (1931) With the exception of the foregoing first four members of the series these metals are stable in dry air but in presence of moisture corrosion occurs in all cases

With the mixed chlorides, prepared from the waste oxides of the thoria manufacture, the product is the so-called "mischmetal" (Ce, 45%, La, Nd, Pr, 35%; Sm, Er, Gd, Y, 20%), which has been used, like aluminium in the Goldschmidt process ("thermite"), to effect the reduction of the refractory oxides of molybdenum, vanadium, niobium (columbium) and tantalum (Muthmann, Hofer, and Weiss, *Annalen*, 1902, 320, 331, 1904, 331, 1, 1905, 337, 370).

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G T M

CEROSIC. A wax derived from sugar cane

CEROSILINE. A wax obtained from the palm tree *Ceroxylon andicolum* Humb. and Bonpl.

CEROTENE, $C_{27}H_{54}$. A crystalline hydrocarbon, m p 63°, found by Konig and Kiesow (Ber. 1873, 6, 500) associated with cholesterol in the fat wax of hay and straw, and detected by Knecht and Hibbert in ordinary household chimney soot (Mem. Manchester Phil. Soc. 1914, 58, [2], 1).

CEROTIC ACID, $C_{25}H_{51}{\cdot}CO_2H$, is found free in beeswax (Brodie, Phil. Trans. 1848, 1, 147, Marie, Ann Chim. Phys. 1896, [vii], 7, 145) and in the dry spores of *Aspidium filix mas* and *Asplenium filix femina* (Kiesel, Ber. 1925, 58, [B], 1386); also found among the products of hydrolysis of wool fat (Grassow, Biochem. Z 1924, 148, 61); as *ceryl cerotate* in insect wax (Brodie, *l.c.*; Henriques, Ber 1897, 30, 1415); in Chinese wax (Gascard, Compt. rend 1920, 170, 1326); in the heavy deposit from sunflower oil, originating in the husk of the sunflower seeds, 30 kg. of the oil yielding 0 14% of the wax (Bareuther, Chem. Umschau. 1923, 30, 117) Cerotic acid has been synthesised by Bleyberg and Ulrich (Ber. 1931, 64, [B], 2504) who record the m.p. 87 7°–87 9°, other values are 82°–82 5° (Gascard, *l c.*), 85°–85 5° (Kiesel, *l c*) The *anhydride* has m p 89 3°–89 5°, the *ethyl* ester m p 59 5°–59 8° (Blyberg and Ulrich, *l c*), the *ceryl* ester m p. 84° (Gascard, *l c*), the *menthyl ester* m.p. 43°, the *phenyl ester* m p 43°, the *anilide* m.p. 97° (Grassow, *l c*), the *thallous* salt is an enantiotropic crystalline liquid having m p 125° and 113°–114° (Walter, Ber 1926, 59, [B], 962).

CEROTIN. Ceryl alcohol, $C_{27}H_{56}O$, m.p 80°. The alcohol obtained by hydrolysing insect wax.

CERULEÏN *v.* ALIZARIN AND ALLIED DYESTUFFS

CERULIGNOL *v* BEECH TAR.

CERUSSITE. Native lead carbonate ($PbCO_3$), of some importance as an ore of lead (Pb, 77 5%), being known as white lead ore It crystallises in the orthorhombic system and is isomorphous with aragonite ($CaCO_3$) and witherite ($BaCO_3$). Six-rayed stellate groups of twinned crystals are extremely characteristic The crystals possess an adamantine lustre, are very heavy (sp gr. 6 5), and effervesce with dilute acid, they are very brittle, breaking with a bright conchoidal fracture, hardness, 3–3½ The mineral occurs in the upper oxidised zones of veins of lead ore, having been formed by the action of carbonated surface waters on galena Enormous deposits of cerussite intermixed with embolite (silver chloro-bromide) and iodyrite (silver iodide) have been extensively mined at Broken Hill in New South Wales, where none of the oxidised ore now remains. Intimately mixed with hemimorphite (hydrated zinc silicate), it is abundant at Broken Hill in Northern Rhodesia. At both of these localities many finely crystallised specimens have been found

L. J. S.

CERVANTITE *v.* ANTIMONY.

CERYL ALCOHOL *v.* CEROTIN.

CETIACOL, *palmiacol*. An insoluble guaiacol preparation used as an antiseptic. It is pyrocatechol methyl cetyl ether.

CÉTINE. A purified spermaceti It is cetyl palmitate

CETOSALOL, *salophen*, acetyl *p* aminophenyl salicylate,

$$HO{\cdot}C_6H_4{\cdot}CO_2C_6H_4{\cdot}NHAc.$$

CETYL ALCOHOL,

$CH_3 \cdot [CH_2]_{16} \cdot CH_2OH$,

occurs as cetyl palmitate in spermacete.

CETYLMALONIC ACID,

$CH_3[CH_2]_{15}CH(CO_2H)_2$.

Prepared by hydrolysing *a*-cyanostearic acid (Hell and Sadomsky, Ber. 1891, 24, 2781), or from ethyl sodiomalonate and cetyl iodide (Guthzeit, Annalen, 1880, 206, 357); m.p. 121·5°–122°.

CEVADILLINE, CEVADINE Alkaloids of the Veratrum Group.

CHAILLETIA TOXICARIA Don. A plant found in Upper Guinea, Sierra Leone, and Senegambia, the seeds of which contain a poisonous resin used for killing rats and other animals (Power and Tutin, J. Amer. Chem. Soc. 1906, 28, 1170).

CHAIRAMIDINE, CHAIRAMINE are Cinchona Alkaloids.

CHALCANTHITE. Native copper sulphate, $CuSO_4,5H_2O$, found as a bright blue efflorescence, or rarely as distinct triclinic crystals, in many copper mines, being especially abundant in some of the Chilean mines. In solution it is always present in the waters issuing from copper mines; these are allowed to flow over scrap iron, the copper being precipitated as cement-copper. About 100 tons of copper have been so saved annually from the waters of the Rio Tinto mine in Spain, and considerable amounts were formerly obtained from the mine waters in Co. Wicklow. L. J. S.

CHALCEDONITE *v.* CHALCEDONY.

CHALCEDONY. A native form of silica occurring as reniform, botryoidal, or stalactitic masses lining and filling cavities in rocks. It is usually greyish or creamy-yellow in colour, and has a characteristic waxy lustre with a certain degree of translucency. It possesses a minutely fibrous structure, the fibres being arranged perpendicularly to the concentric banding of the material. The optical character and orientation of the fibres is variable; and based on these differences French authors have distinguished several forms of silica under special names (quartzine, lutecite, lussatite, chalcedonite, and pseudochalcedonite). The physical characters of the mineral approach those of quartz, but with slightly lower values; sp.gr. 2·57–2·64; hardness 6½–7; n_{Na} 1·5325, 1·5435. Analyses show, in addition to silica, the presence of variable amounts of impurities (iron oxides, alumina, etc.), and on the average about 1% of water. The water is probably present as adsorbed water held between the fibres; and its presence supports the idea that the mineral was deposited in a colloidal form as hydrated silica, and that it afterwards passed into minutely crystalline quartz. The name "enhydros" is given to hollow nodules of chalcedony containing water and an air bubble which is visible through the semi-transparent wall. Depending on the nature of the impurities present (and partly also on the state of aggregation of the material) the mineral may be of various colours, and on these differences are based several trivial varieties which are used as semi-precious stones. *Carnelian* owes its red colour to ferric oxide, and *sard* its brown colour to hydrated ferric oxide; sard passes over into carnelian when ignited. The apple-green colour of *chrysoprase* is due to nickel silicate and the dark green of *plasma* to an iron silicate. *Heliotrope* shows blood-red spots on a dark green ground. Smoke-grey *flint* passes imperceptibly into more typical chalcedony. In *agate* differently coloured layers are banded together in the same stone. The uses of chalcedony are the same as those of agate (*q.v.*). On the artificial colouring of chalcedony, *v.* AGATE.

L. J. S.

CHALCOPYRITE or **COPPER-PYRITES** (Ger. *Chalkopyrit, Kupferkies*). A sulphide of copper and iron, $CuFeS_2$, containing when pure 34·5% of copper, and the most important of the ores of copper. It has a characteristic brassy-yellow colour with metallic lustre, and on the surfaces often displays a brilliant iridescent tarnish (peacock-copper-ore). It often occurs together with, and intimately intermixed with, iron-pyrites, from which it can be distinguished by its deeper colour and lower degree of hardness; copper-pyrites (H. 3½–4) is readily scratched with a knife, giving a greenish-black powder, whilst iron-pyrites (H. 6–6½) is scratched only with difficulty or not at all. It occurs in mineral-veins and in bedded deposits, and by its alteration gives rise to many secondary copper minerals. Crystals are tetragonal with inclined hemihedrism and complex twinning, but only rarely are they distinctly developed; sp.gr. 4·2. L. J. S.

CHALCOSINE, CHALCOCITE, or **COPPER-GLANCE** (Fr. *Chalcosine*, Ger. *Chalkosin*, Span. *Chalcosina*). Native cuprous sulphide, Cu_2S, crystallising in the orthorhombic system. Excellent twinned crystals were formerly found in some abundance in the neighbourhood of Redruth in Cornwall (hence the name redruthite) and Bristol in Connecticut; usually, however, the mineral is found as compact masses. It is iron-black with metallic lustre, but, on exposure to light, it soon becomes dull with a powdery black coating. It is soft (H. 2½) and sectile, and can be readily cut with a knife; sp.gr. 5·7. It is of wide distribution in veins of copper ore, and is often of importance as an ore, especially when it contains small amounts of silver. Frequently it occurs intimately intergrown with other copper sulphide minerals—chalcopyrite, bornite, and covelline.

A cubic modification of Cu_2S is stable above 91°C. Several varieties of chalcosine have been distinguished by metallographic methods. A lamellar structure is taken to indicate that the mineral was originally deposited in the cubic form at a temperature higher than 91°, which on cooling changed over into a twinned aggregate of orthorhombic crystals. Distinctly formed paramorphs with cubic outlines (as with leucite) are, however, not known.

The name chalcosine (F. S. Beudant, 1832) was changed to chalcocite by J. D. Dana (1868) without sufficient reason, the letter c here having three different values.

Isomorphous with chalcosine is the mineral *stromeyerite* $(Ag,Cu)_2S$, which has been found in considerable quantities in the Altai Mountains in Siberia. L. J. S.

CHALCOSTIBITE or WOLFSBERGITE. A mineral of the composition

$$Cu_2S{\cdot}Sb_2S_3{=}CuSbS_2,$$

found as small orthorhombic crystals at Wolfsberg in the Harz Mountains, Guejar in Spain ("guejarite"), and Bolivia More recently large crystals have been found in the wadi Cherrat in Morocco. The crystals have a perfect cleavage in one direction ; sp gr. 5 0, hardness 3–4. The mineral has been recognised by metallographic methods from several other localities, and it is no doubt of wide distribution in copper ores Massive material from Bolivia gave Ge 0 91%. L J S

CHALCOTRICHITE, *cuprite* Native cuprous oxide.

CHALK. A white or greyish, loosely coherent kind of limestone rock, composed almost entirely of the calcareous remains of minute marine organisms (foraminifera, coccoliths, etc), and fragments of shells The purest kinds contain up to 99% of calcium carbonate in the form of the mineral calcite Silica is always present in small amounts as the mineral opal, representing the remains of other minute marine organisms (radiolaria, etc) and sponge spicules , and it is often segregated as the nodular masses of flint so commonly found embedded in chalk rock. Minute grains of quartz, felspar, zircon, rutile, and other minerals are also often present With the admixture of clayey material there may be an insensible gradation from pure chalk to *chalk marl*. In *phosphatic chalk* there is much calcium phosphate (up to 45%) , in green *glauconitic chalk* there is an admixture of grains of glauconite (a hydrated iron potassium silicate), and in *red chalk* there is some iron hydroxide Not only may there be considerable variations in the composition of chalk, but there may also be wide variations in the colour (snow-white, grey, etc.), and texture of the material It may be soft, incoherent, and porous, or quite hard and crystalline (as the chalk of the Yorkshire coast).

The following analyses of chalk are selected from those quoted by A J. Jukes Browne, "The Cretaceous Rocks of Britain," Mem. Geol. Survey, 1903 (*q v.* for details respecting the English chalk) , I, Middle Chalk from Wye, Kent ; II, Chalk Rock from Boxmoor, Hertfordshire ; III, soft white Upper Chalk from Farnham, Surrey :

	I.	II	III
CaO	52 750	54 900	53 18
MgO	0 211	0 374	0 30
Fe_2O_3	0 067	0 347	0 40
Al_2O_3	0 113		
MnO	0 140	—	—
K_2O	0 098	—	0 22
Na_2O	0 013	—	0 21
CO_2	37 670	42 101	42 37
P_2O_5	0 106	0 713	0 08
SO_3	0 082	0 465	0 09
Cl	0 006	—	—
SiO_2 (soluble)	0 035	0 128	—
H_2O Organic matter	5 400	—	—
Insoluble	2 480	1 003	0 87
	99 180	100 031	99 92
$CaCO_3$	85 61	97 001	95 76

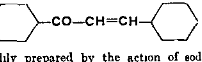
The uses of chalk are numerous For example, as a writing material in form of white and coloured crayons ; for the manufacture of quicklime, mortar, Portland cement, plaster, etc , and as a fertiliser. Whiting is prepared by grinding chalk and collecting the finer sediments from water ; this is used for polishing, making putty, and many other purposes. Under the name of "Paris white," chalk is used in the manufacture of india rubber goods, oilcloth, wallpaper, etc. The harder kinds are extensively used as a building stone.

Large quantities of chalk are quarried in the counties of Kent, Surrey, Sussex, Cambridge, Lincoln and Hampshire ; Kent being by far the most important. The production of English chalk is six to seven million tons per annum A certain amount of this is exported to the United States, though there are extensive beds of chalk in Kansas, Arkansas and Texas.

L. J. S.

CHALK, FRENCH, $H_2Mg_3Si_4O_{12}$ Talc, steatite, or soapstone.

CHALKONE GROUP. *Challone* or benzylideneacetophenone,

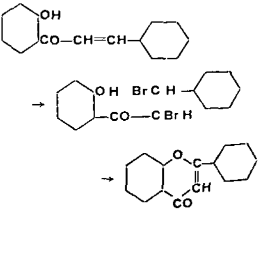


is readily prepared by the action of sodium hydroxide on an alcoholic solution of benzaldehyde and acetophenone at ordinary temperature. It consists of yellow rhombic prisms, m p. 57°–58°, and when submitted to hydrolysis is reconverted into the aldehyde and ketone

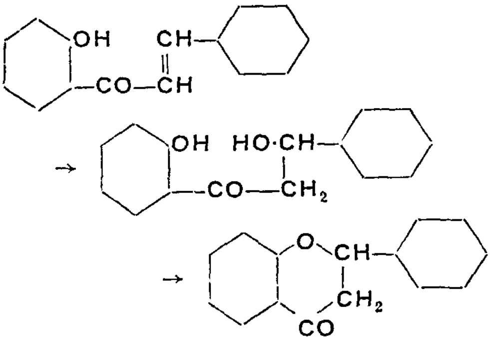
By the employment of hydroxyacetophenones and hydroxybenzaldehydes, in general previously methylated, numerous chalkone derivatives were synthesised by von Kostanecki and his co workers (Ber. 1898, *et seq.*).

Of the various derivatives, the 2-hydroxy chalkones possess great interest on account of their relationship to the naturally occurring dyestuffs of the flavone and flavonol groups

2 *Hydroxychalkone*, yellow needles, m p. 88°–89°, dissolves in alkali hydroxides with an orange colour, and in concentrated sulphuric acid with a yellow colour (Feuerstein and von Kostanecki, *ibid* 1898, 31, 715). It is converted into flavone by the action of alkali hydroxides on the dibromo addition product of its acetyl derivative (Feuerstein and von Kostanecki, *ibid.* 1738):



When 2-hydroxychalkone is digested at the boil with alcoholic sulphuric acid, *flavanone (dihydroflavone)* is produced:



and this method is generally adoped for the synthesis of flavanone derivatives. On hydrolysis the flavanones yield chalkones, a reversal of the above reaction. In these cases the reaction is not unidirectional, and the conversion of flavanone into chalkone, or chalkone into flavanone, is never complete.

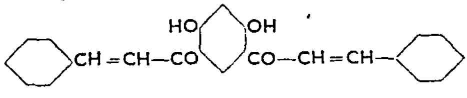
Though as a rule a chalkone only is obtained by the interaction of aldehyde and hydroxyketone, when gallacetophenone dimethyl ether (Woker, von Kostanecki, and Tambor, *ibid.* 1903, 36, 4235) or quinacetophenone monomethyl ether (von Kostanecki and Lampe, *ibid.* 1904, 37, 773) is condensed with benzaldehyde in the presence of sodium hydroxide, 7:8-dimethoxy- and 6-methoxy-flavanone, respectively, are thus directly produced. Again, Löwenbein (*ibid.* 1924, 57, [B], 1515) obtained flavanone in 80% yield by adding excess of aqueous sodium hydroxide to a warm alcoholic solution of *o*-hydroxychalkone.

Simonis and Lear (*ibid.* 1926, **59** [B], 2908) observe that phenolic ethers, particularly those containing a substituent in the *para*-position to the alkoxyl-group, are converted by suitable acid chlorides in the presence of aluminium chloride (1 mol.) into alkylated chalkones; the use of a further molecule of aluminium chloride removes the alkyl group. Thus, quinol dimethyl ether, cinnamoyl chloride, and aluminium chloride (1 mol.) yield 2:5-dimethoxyphenyl styryl ketone, and this is converted by a further molecule of aluminium chloride into the 5-methoxy- compound, which, with alkali hydroxide, gives 6-methoxyflavanone. Monti (Gazzetta, 1930, **60**, 43) points out that this method is not new (*cf.* Stockhausen and Gattermann, Ber. 1892, 25, 3535). Shinoda and Sato (J. Pharm. Soc. Japan, 1928, 48, No. 558, 109) have synthesised chalkones, hydrochalkones, and flavanones by a similar method.

By employing the fully benzoylated derivatives, Russell (J.C.S. 1934, 218, 1066, 1506) has synthesised chalkones by condensing hydroxyacetophenones with hydroxybenzaldehydes in dry ethyl acetate at 0° in presence of hydrogen chloride.

o-Hydroxychalkones are converted into flavones by oxidation with selenium dioxide (Mahal, Rai, and Venkataraman, *idid.* 1935, 866), whilst by oxidation with alkaline hydrogen peroxide, flavonols are produced (Algar and Flynn, Proc. Roy. Irish Acad. 1934, Ser. B, 42, separate issue).

Ryan and O'Neill (Proc. Roy. Irish Acad. 1915, 32, 48, 167) obtained *di-o-hydroxydichalkone (dibenzylidenediacetoresorcinol)*:



yellow crystals, m.p. 196°–198°, by interaction of diacetoresorcinol dimethyl ether and benzaldehyde, and demethylation of the product. An interesting fact recorded by these authors is that, by a variation in its method of preparation, four distinct varieties of this dichalkone can be produced. Whereas three of these, designated as α, β, and δ, are stereo-isomers, the fourth or γ variety is structurally related to the other three. A. G. P. and E. J. C.

CHALMERSITE *v.* CUBANITE.

CHALYBITE. Native iron carbonate, $FeCO_3$, forming rhombohedral crystals isomorphous with calcite ($CaCO_3$), and of importance as an ore of iron. It is often known as *siderite* but this name had earlier been applied to three other mineral species; it has also been applied to lodestone, ironstone and ironwort, and at the present time it is in common use as a group name for meteoric irons. *Siderose* was the original form of the name as applied by F. S. Beudant in 1832 to iron carbonate. Sp.gr. 3·9; hardness, 3½. Small, brilliant crystals of varying habit are common in many mineral veins, for example those of Cornwall. Veins of massive sparry material showing cleavage surfaces (*Spathic iron-ore*) have been mined in the Brendon Hills in Somersetshire, Weardale in Co. Durham, the Siegen district in Westphalia, dep. Isère in France, etc. The fresh, unaltered material is creamy white in colour ("white ore"), but when slightly weathered it is brown ("brown ore"). The Cleveland ore is a pisolitic form of chalybite occurring as beds in the Lias strata; and the important *clay-iron-stone* and *black-band iron-stone* of the Coal-measures consist of compact chalybite, intermixed with clay and carbonaceous matter. A nodular form with an internal radiated structure is known as *sphærosiderite.*

	I.	II.	III.	IV.
FeO . . .	61·08	49·47	39·92	46·35
Fe_2O_3 . . .	—	—	3·60	3·00
Al_2O_3 . . .	—	trace	7·86	0·30
MnO . . .	1·12	2·42	0·95	1·61
CaO . . .	0·10	3·47	7·44	1·93
MgO . . .	0·13	3·15	3·82	2·24
CO_2 . . .	38·19	37·71	22·85	32·46
P_2O_5 . . .	—	trace	1·86	0·67
SiO_2 . . .	—	1·20	7·12	—
SO_3. . . .	—	trace	trace	trace
FeS_2 . . .	—	0·08	0·11	0·15
H_2O . . .	—	—	2·97	1·43
Organic matter	—	trace	trace	2·95
Insoluble . .	—	3·77	1·64	7·29
	100·62	101·27	100·41	100·38
Total Fe . .	—	38·56	33·62	38·29

Analysis I is of pure selected crystals from near Camborne, Cornwall (A. Hutchinson, Min. Mag. 1903, 13, 209); II–IV of ores, by A. Dick, in "Iron Ores of Great Britain," Mem Geol. Survey, 1856–1862; II yellowish grey spathose ore from Weardale; III greenish-grey earthy oolitic ore from Cleveland (also K_2O 0 27 in the portion soluble in HCl); IV clay-iron stone from Shelton colliery, Hanley, Staffordshire. L. J S

CHAMOMILE, ESSENTIAL OIL OF. The oil distilled from the flowers of the Roman chamomile *Anthemis nobilis*, L. (Fam Compositæ) indigenous to Great Britain, Southern Europe, Spain, and Italy. The flowers mature in August. When freshly distilled the oil is a deep blue colour, which gradually fades to a greenish-yellow colour on keeping The yield is about 1·0%.

Constituents —Ethyl *iso*butyrate, angelic, and tiglic esters of *iso*butyl and hexyl alcohols and anthemol, an alcohol belonging to the terpene series. The blue constituent is *chamazulene*

Characters —Sp gr at 15 5° 0 905–0 915, a_D^{20} −1° to +3°, n_D^{20} 1 442–1·465 Soluble in *6 vols of 70% alcohol* German chamomile oil obtained from the flowers of the German chamomile *Matricaria Chamomilla*, L, has sp gr. 0 930–0 940, congeals about +1, and is soluble in 3 vols of 90% alcohol It contains chamomillol, trichamomillol, esters of caproic acid, solid hydrocarbons, furfuraldehyde, and umbelliferone methyl ether It also has a blue colour due to the presence of chamazulene C T B

CHAMOMILE FLOWERS. According to Power and Browning (J C S. 1914, 105, 1833), the flowers of *Anthemis nobilis* Linn contain, in addition to numerous other substances, an apigenin glucoside, $C_{21}H_{20}O_{10},2H_2O$, faintly yellow microscopic crystals, m p 178°–180°. It dissolves in alkalis with a yellow colour and gives with aqueous ferric chloride a purplish-brown coloration Dried at 125°–130° it loses 1 mol of water of crystallisation, but the second molecule cannot be eliminated without decomposing the substance. This is evident from the composition of the *hexa acetyl* derivative, $C_{21}H_{14}O_{10}(CO\,CH_3)_6$, colourless microscopic crystals, m p. 144°–146°, the molecule of water in question being eliminated in the process of acetylation.

When hydrolysed, the glucoside yields apigenin 1 3 4′ *trihydroxyflavone* and dextrose.

A. G. P. and E J. C.

CHAMOSITE. An ore of iron, closely allied to *thuringite*,

$$H_{18}Fe''_8(Al,Fe''')_8Si_6O_{41}$$

CHAMOTTE. This term, more frequently used on the Continent than in this country, is applied to the non plastic component incorporated with raw clays, and is almost synonymous with the English term "grog" On the Continent, clays are often carefully selected and burned in special furnaces (*e g* shaft or rotary kilns) to yield a thoroughly fire-shrunk material, which mixed with raw clay reduces shrinkage, prevents warping, and facilitates drying, etc. In some cases, such chamotte forms the main constituent of the refractory, the necessary binding power being secured by the use of a highly plastic clay, such as a "ball clay." In this country, discarded furnace blocks, crucibles, etc., are broken up and used generally as grog. The term chamotte more often implies a selected clay, specially burned for the purpose. W. C. H.

CHANNA, a mesembrine alkaloid.

CH'AN SU *v.* CARDIAC GLYCOSIDES, Toad Poisons.

CHARCOAL *v.* CARBON.

CHARD. A species of beet (*Beta vulgaris* var. *cicla*) the leaves and leaf stems of which are boiled as a vegetable. Other names include "Swiss chard" and "leaf beet." Chung and Ripperton (Hawaii Agric. Exp Sta. Bull. 1929, No 60) record the following analyses of the edible portion: H_2O 92 2, protein 1 45, fat 0 2, N free extract 3 1, fibre 0 9, ash 2 2%. The mineral constituents include Ca 0 10, Fe 0 004, P 0 024 %, and Cu 1·1 mg per kg A. G. Po.

CHARTREUSE. A well known and popular liqueur, the original recipe for which is said to have been presented by the Marquess d'Estrees to the Carthusian monks of Paris in 1602. Owing to the difficulty of procuring the necessary alpine plants in that neighbourhood it was passed on to members of the order at La Grande Chartreuse near Grenoble in 1735 The *elixir vitæ* was valued as a stimulant for the less robust members of the fraternity weakened by age or by the privations and hardships entailed by the severity of their religious exercises and was also dispensed to the feeble poor of the district.

After numerous disasters, occasioned by fire, pillage, and confiscation of their property through religious and political persecutions, culminating in the loss of everything during the French Revolution, the monastery was restored in 1816 although in a very impoverished condition The secret of the manufacture of the "elixir" had, however, been carefully preserved, and this was made the basis of the recipes for other varieties of liqueur The two main varieties are named in accordance with their colours "green" and "yellow," but a colourless liqueur known as "white" chartreuse also enjoys considerable favour. The virtues of these preparations were widely advertised by the military officers who were quartered in the monastic buildings about the middle of last century and in consequence the monks entered upon an era of unprecedented prosperity. To meet the greatly increased demand extensive and modern plant was installed at Fourvoirie in 1863 In 1906, however, there fell upon the fraternity further trouble in the passing of the French Religious Associations Act. In consequence, the monks migrated across the border to Tarragona in Spain where they have since continued the manufacture of liqueurs according to their old formulæ.

More than 200 ingredients are said to be used in the manufacture of genuine chartreuse and its spirit basis is rectified grape spirit distilled from sound wine. The usual alcoholic strength of each of the three varieties of

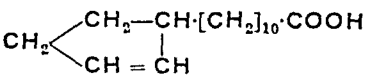
chartreuse is respectively: *green* 55% of alcohol by volume or 96% of proof spirit; *yellow* 42·5% of alcohol or 74·5% of proof spirit; *white* 30% of alcohol or 52·5% of proof spirit.

There are many imitations of chartreuse, mostly prepared from plain spirit flavoured with essential oils and coloured by means of the various ingredients described under Cordials and Liqueurs. The formulæ given in the attached table are typical of those adopted in the preparation of these imitations. The mixture is digested for 24 hours and then distilled until nearly all the spirit is over. The distillate is diluted to 100 litres, coloured, and sweetened with sugar as desired, and, after standing for some time, filtered.

Ingredients.	Green.	Yellow.	White.
China cinnamon	15 g.	15 g.	125 g.
Mace . . .	15 ,,	15 ,,	30 ,,
Lemon balm, dried . . .	500 ,,	250 ,,	250 ,,
Hyssop (flower tops) . . .	250 ,,	125 ,,	135 ,,
Peppermint (dried) . .	250 ,,	—	—
Thyme . . .	30 ,,	—	—
Balsime (Bal major) . .	125 ,,	—	—
Juniper . . .	250 ,,	125 ,,	125 ,,
Arnica (flowers).	10 ,,	15 ,,	—
Balsam poplar (buds) . .	15 ,,	—	—
Angelica (seeds)	125 ,,	125 ,,	125 ,,
Angelica (roots).	62·5 g.	30 ,,	30 ,,
Coriander . .	—	1,500 ,,	—
Cloves . . .	—	15 ,,	30 ,,
Aloes (Socotrine)	—	30 ,,	—
Cardamom (small) . .	—	50 ,,	30 ,,
Nutmegs . .	—	—	15 ,,
Calamus . .	—	—	300 ,,
Tonka beans .	—	—	15 ,,
Alcohol (85%) .	62·5 litres	42·5 litres	52·5 litres
White sugar. .	25·0 kg.	25·0 kg.	37·5 kg.

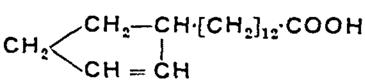
F. G. H. T.

CHAULMOOGRA (CHAULMUGRA) OIL GROUP. This group of oils, obtained from the seeds of certain tropical species of the Fam. Flacourtiaceæ Warburg (*syn.* Bixineæ, Bixaceæ Bentham and Hooker) is remarkable on account of the presence in predominating quantity of the glycerides of the optically active (dextrorotatory) chaulmoogric and hydnocarpic acids. These acids, discovered by Power and his collaborators (J.C.S. 1904, **85**, 838, 851; 1905, **87**, 884; 1907, **91**, 557), are characterised by the presence of a cyclopentene nucleus, and their formulation by Power as follows,



Hydnocarpic acid. $C_{16}H_{28}O_2$,

and



Chaulmoogric acid, $C_{18}H_{32}O_2$,

has been confirmed by synthesis of the *dl*- forms of the acids (*cf.* Perkins and Cruz, J. Amer. Chem. Soc. 1927, **49**, 1070; R. Adams and collaborators, *ibid.* 1926, **48**, 1080).

Derivatives of these acids, including the oils themselves (*i.e.* the glyceryl esters), all possess remarkable therapeutic value in the treatment of leprosy, and the use of the oils for this purpose, which has been native practice from olden times in India and Indo-China, has extended within the last 20–30 years all over the world with marked success. The employment of chaulmoogra oils in the treatment of tuberculosis has also been mooted (*cf.* Schöbl, Philippine J. Sci. 1923–1924; Peirier, Thesis, Marseille, 1930; Graham and co-workers, Illinois Agric. Expt. Sta. 47th Ann. Rept. 1935 (1933–1934), 86).

As a result of the work of V. G. Heiser, and especially of Leonard Rogers in India (1916–1917) and of Dean and Hollmann in Honolulu, the old method of oral administration of the oils (which is limited by the nauseating properties of the oils) has been superseded by injection of the sodium salts, or of the ethyl esters of the fatty acids of the oils. Of a further series of derivatives of chaulmoogric acid, prepared by West (*cf.* Philippine J. Sci. 1927–1929), none appears to offer any marked therapeutic advantage.

(For reviews concerning the therapeutic applications of chaulmoogra oil, *cf.* Hollman and Dean, J. Cutan. Dis. 1919, **37**, 367; Muir, "Leprosy—Diagnosis, Treatment and Prevention," Lahore, 1928, 4th ed.; Schlossberger, Z. angew Chem. 1924, **37**, 4; Wayson and Badger, U.S. Pub. Health Rep. 1928, **43**, 2883; (discussion) Proc. Roy. Soc. Med. 1927, **20**, 997; Eubanas, J. Philippine Is. Med. Assoc. 1931, **10**, 203; Findlay, "Recent Advances in Chemotherapy," London, 1930; Fischl and Schlossberger "Handbuch der Chemotherapie," Vol. I, Leipzig, 1932; and the literature of tropical medicine.)

For medicinal purposes, the cold-pressed oils are used. Suitable methods of refining are described by Perkins, Cruz, and Reyes Ind. Eng. Chem. 1927, **19**, 939.

Among the best-known oils of the chaulmoogra group are those from seeds of three Asiatic species, viz. chaulmoogra oil from *Taraktogenos Kurzii* King (*Hydnocarpus Kurzii* Warb.); lukrabo or krabao oil from *Hydnocarpus anthelminticus* Pierre; and hydnocarpus oil from *Hydnocarpus Wightiana* Blume, whose properties, together with those of the oils from *H. alcalae* de Candolle and *Carpotroche brasiliensis* Endl. are illustrated in Table I, p. 522.

Similarly active oils, which differ from each other in their respective contents of chaulmoogric and hydnocarpic acids, are obtained from several other (but not all) species of the genera *Hydnocarpus*, *Taraktogenos*, and *Asteriastigma* from Asia and Oceania, *Caloncoba* from Africa, and *Carpotroche*, *Lindackeria*, and *Mayna* from South America (Brazil).

These oils appear as soft yellowish or brownish fats at ordinary temperatures (15°–20°C.): they melt between 22° and 30°C., and show optical rotations ranging from $[\alpha]_D$=about +43° to +64° at 30°C. (in $CHCl_3$); their

TABLE I.—CHARACTERISTICS OF OILS OF THE CHAULMOOGRA GROUP[1]

	Taraktogenos Kurzii[2]	*Hydnocarpus anthelmintica*	*Hydnocarpus Wightiana*[3]	*Hydnocarpus alcalae*	*Carpotroche brasiliensis*
Sp gr $\frac{30°}{40°}$	0·943–0·954 (0·940–0·960/25°C.)	0·943–0·954	— (0·95–0·96/25°C.)	0·944–0·954	0·955–0·959
n_D	1·472–1·477/30°C.	1·4715–1·4753/30°C.	1·4759–1·4783/30°C (1·472–1·476/40°C.)	1·4763–1·477/30°C.	1·4792–1·4818/25°C
$[\alpha]_D^{30}$ (in $CHCl_3$)	+38° to +55° (+48° to +60° at 25°C.)	+42·5° to +51·5°	+51° to +58° (≮ +53°.)	+46·3° to +49·6°	+52° to +59°/20°C
M p.	22°–26°C (c 25°C.)	20°–30°C. (mostly 20°–26°C.)	22°–32°C (20°–25°C.)	About 30°C	21°–23°C
Acid value	10–28 (≯22·4)	1–20	0–20 (≯25)	1–13	0–7
Saponification value	183–215 (196–213)	187–226·5 (usually 200–210)	197–207 (198–204)	189–202	201–205
Iodine value	94–113 (93–104)	81–99·6	95–103 (97–103)	84–94	101·6–112·1
T p of fatty acids	32°–40°C	36°–42°C	39·5°–42°C	55°C	m p 29·5°C

[1] The analytical characteristics of each oil vary somewhat according to the origin and condition of the seeds the figures reproduced above are typical of the usual ranges, but do not necessarily include extreme values that have been reported in isolated cases

[2] Limits specified by "United States Pharmacopœia," XI (1936), shown in brackets (N B—The "United States Pharmacopœia," XI, admits under the title of *Oleum Chaulmoogræ*, the oils from *T Kurzii*, *Hydnocarpus Wightiana*, *H anthelmintica*, or other species of *Hydnocarpus* in so far as they conform to the specified requirements.)

[3] Limits specified by "British Pharmacopœia," 1932, shown in brackets

saponification values lie, as a rule, between 197 and 215, and the iodine values between 82 and 105, the content of unsaponifiable matter is low, *e g* 0·2% (For descriptions of a number of *Hydnocarpus* and related oils, *see* Perkins and Cruz, Philippine J. Sci 1923, 23, 543; Perkins, Cruz and Reyes Ind. Eng Chem 1927, 19, 939; André, Compt rend 1925, 181, 1089 (extracted oils); Rock, U.S. Dept. Agric. Bull No. 1057, 1922, Marcan, J S C.I. 1926, 45, 305T; Peacock and Aiyar, Burmese Forest Bull No 21, 1930, Perrier, J. Pharm. Chim. 1929, (viii), 10, 124, *also* Thesis, Marseille, 1930 (African sp); Kuhlmann, Mem. Inst. Oswaldo Cruz (Brazil), 1928, 21, 389; M. T. François, Bull Sci. Pharmacol. 1935, 42, 24).

(It may be noted, however, that the oils from certain species attributed to the above genera as well as oils from other genera of Flacourtiaceæ, *e g.* from *Oncoba spinosa* Forsk., *Gynocardia odorata* Brown (Gynocardia oil), which have occasionally been confused with the true chaulmoogra, show no optical activity and contain no cyclic acids, *cf.* Power, *l c.*; Pyman, Repts. Progress Appl. Chem. 1916, 1, 292.)

In many cases the seeds of the chaulmoogra group contain a cyanogenetic glucoside.

Chaulmoogra oil, which was formerly officinal in England, consists almost entirely of the glycerides *chaulmoogro-di-hydnocarpin* and *hydnocarpo dichaulmoogrin*, in proportions of about 6 1 (*cf* Bömer and Engels, Z Unters Lebensm. 1929, 57, 113), a small proportion of another glyceride, probably tripalmitin or stearopalmitin, was also isolated Correspondingly, the fatty acids of chaulmoogra oil consist of about 55–60% of hydnocarpic acid, and about 40% of chaulmoogric acid, together with a small amount of palmitic acid Small amounts of a liquid optically active acid (possibly a lower homologue (C_{14}?) of hydnocarpic acid, or a more unsaturated cyclic, C_{18}-acid such as gorlic acid (*see below*) have also been found in chaulmoogra oil itself and in other oils of the group (*cf* Perkins and Cruz, *l c.* 1923, Wrenshall and Dean, U.S. Publ. Health Service Bull. 1924, 141, 12, André, *l c*).

The occurrence of small amounts of "taraktogenic acid," $C_{36}H_{60}O_6$, "isogadoleic acid," $C_{20}H_{38}O_2$, and the lactonic "paralinolic acid," $C_{18}H_{32}O_2$, reported by Hashimoto (J Amer. Chem. Soc. 1925, 47, 2325) requires confirmation.

The proportion of hydnocarpic acid is higher in lukrabo oil, which constitutes the *Oleum Hydnocarpæ* ("taifushi oil") of the "Japanese Pharmacopœia," and in Hydnocarpus oil (also known in India as "kavatel" or "marotti" oil), which, as the *Oleum Hydnocarpi* of the 1932 "British Pharmacopœia" has replaced the *Ol. Chaulmoogræ* of the earlier edition. (The cold expressed oil is specified by the "British Pharmacopœia.") Hydnocarpus fruits

arrive on the market in a better condition than chaulmoogra fruits, and consequently a better quality of oil can be recovered ; the higher proportion of hydnocarpic acid is also advantageous, since this acid appears to be slightly more active therapeutically than chaulmoogric acid. Further, owing to the almost total absence of palmitic acid, which distinguishes this oil from chaulmoogra oil, hydnocarpus oil forms the most convenient material for the preparation (in high yield) of pure hydnocarpic acid (*cf.* Perkins, Cruz, and Reyes, *l.c.* 1927 ; Georgi, Dept. Agric. S.S. and F.M.S. Sci. Series, 1932, No. 9; Marcan, *l.c.*; Cole and Cardoso, J. Amer. Chem. Soc. 1937, **59**, 963).

Perkins was not able to detect any lower homologue of hydnocarpic acid in hydnocarpus oil, but small quantities of a liquid optically-active acid (gorlic acid ?) have been isolated at the Imperial Institute (Bull. Imp. Inst. 1936, **34**, 145 ; Nigerian oil) and by Cole (Philippine J. Sci. 1929, **40**, 499) ; the latter also reports the presence of about 1% of lauric (?) acid.

Hydnocarpus oil, like chaulmoogra oil, has usually been described (*cf.* Brit. Pharm. 1932) as almost wholly soluble in hot 90% alcohol, and partially soluble in the cold ; it seems possible, however, that this only applies to oils containing a considerable proportion of free fatty acids (as is the case with crude commercial oils) since a sample of almost neutral hydnocarpus oil (acid value 1·2) examined at the Imperial Institute (*l.c.*) did not exhibit this property, although it was normal in all other respects. In 1911 a certain amount of marotti oil found its way into Germany under the misnomer of "cardamom oil," and, its toxic properties being apparently overlooked, was used in margarine with disastrous results (*cf.* Reinsch, Chem.-Ztg. 1911, **35**, 77).

The oil from the seeds of the Philippine *Hydnocarpus alcalae* De Candolle ("dudu-dudu"), which contains much chaulmoogric acid (*c.* 90% of the total acids), but very little hydnocarpic acid (*cf.* Brill, J. Philippine Sci. 1917, **12**, A, 37 ; Santos and West, *ibid.* 1929, **40**, 485), and the Brazilian **carpotroche oil** from *Carpotroche brasiliensis* Endl., which contains both hydnocarpic and chaulmoogric acids (*cf.* Rothe and Surerus, Rev. brasil. Chim. 1931, **2**, 358 ; D. da Silva, Rev. brasil. Med. Pharm. 1926, **2**, 627 ; Jamieson, Drug Markets, 1931, **29**, 350), are used locally in the treatment of leprosy. In Africa, **gorli (gorley) seed oil** (from *Caloncoba echinata* Oliv. Gilg.=*Oncoba echinata* Oliv.) is used ; this oil contains about 80% of chaulmoogric acid, palmitic acid, and also a more unsaturated acid of the cyclic series, **gorlic acid**, $C_{18}H_{30}O_2$ (*cf.* Goulding and Ackers, J.C.S. 1913, **103**, 347) ; André and Jouatte, Bull. Soc. chim. 1928, (iv), **43**, 347; Paget, J.C.S. 1937, 955). The oils of *H. alcalae* and *C. echinata* are convenient materials for the preparation of pure chaulmoogric acid (Cole and Cardoso, *l.c.*).

In the Belgian Congo, representatives of the chaulmoogra group (*cf.* E. de Wildeman, Bull. Inst. Roy. Col. Belge, 1930, I, (1), 94), include *Caloncoba Welwitschii* Oliv. Gilg. It is interesting to note that although the oil from the seeds is rich in cyclic acids (*cf.* Peirier, *l.c.*), the fat obtained from the fruit-pulp which surrounds the seeds is optically inactive, and consists apparently of glycerides of stearic, palmitic, and oleic acids (Adriaens, Bull. Inst. Roy. Col. Belge, 1932, III, (2), 373, 389).

E. L.

CHAULMOOGRIC ACID, $C_{18}H_{32}O_2$. An unsaturated acid found by Power and Gornall among the fatty acids contained in chaulmoogra oil from *Taraktogenos Kurzii* King. Optically active $[\alpha]_D$ +56° ; m.p. 68°; b.p. 247°–248°(corr.)/20 mm. Easily soluble in chloroform and ether. Forms readily crystallisable salts with metallic bases, and esters with aliphatic radicals (J.C.S. 1904, **85**, 838, 851).

CHAVICIN, a resin occurring in pepper.

CHAY-AVER *v.* CHAYROOT.

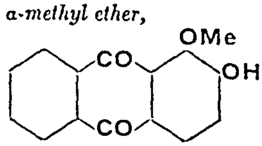
CHAY ROOT. Chay root or Chay-aver (from *chaya*=which fixes colour, and *ver*=root), also called Indian madder, is the root of *Oldenlandia umbellata* Linn. (Fam. Rubiaceæ), a small bush or herb found on sandy soils chiefly near the sea-coast. The plant occurs in North Burma and Ceylon, but is most abundant in certain tracts of the Madras Presidency, from Orissa southwards. It is or was extensively cultivated on the Malabar and Coromandel coasts, especially the latter, and employed in dyeing a colour analogous to Turkey-red. The roots are usually about 10–12 ins. long and ¼ in. thick, somewhat straight and stiff, tough and wiry, and with few or no lateral fibres. When freshly gathered they have an orange colour, but when dried and kept they assume a yellowish-grey hue. The colouring principles seem to reside chiefly, if not entirely, in the bark of the root.

A short account of the history of chay root and its application to the fibres is given in the papers of Hummel and Perkin (J.C.S. 1893, **63**, 1160; J.S.C.I. 1894, **13**, 346).

Chay root resembles madder in that both contain ruberythric acid, alizarin, rubichloric acid, and cane sugar ; on the other hand, purpurin, purpurin- and purpuroxanthin-carboxylic acids, which are present in madder, are entirely absent in chay root. Again, whereas only traces of yellow crystalline substances are found in madder, chay root contains considerable quantities of yellow crystalline compounds which are quite distinct from those present in madder.

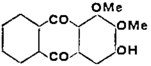
The phenolic constituents of chay root have been studied by the sulphurous acid extraction method, and also by a subsequent exhaustion of the residual root with boiling lime water (Hummel and Perkin, *l.c.*; J.C.S. 1895, **67**, 817; Perkin, *ibid.* 1907, **91**, 2066). There was thus obtained, in addition to chlororubine and alizarin, a mixture of non-tinctorial yellow substances which are present (probably as glucosides) in comparatively large amount (1%). These consist principally, if not entirely, of the following substances :

Alizarin α-methyl ether,

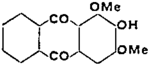


long orange-yellow needles, m p. 178°–179°, is readily converted into alizarin, for prolonged digestion with boiling baryta water is sufficient to hydrolyse the methoxyl group. This property of the α-methoxyl group probably accounts for the failure to obtain this compound, or the dimethyl ether, by digestion of alizarin with methyl iodide and alkali. The synthesis of alizarin α-methyl ether was effected (Oesch and Perkin, Chem. Soc. Proc. 1914, 30, 213) by the action of diazomethane on β-acetylalizarin, whereby a mixture of β-acetylalizarin α methyl ether and α acetylalizarin β-methyl ether was produced, migration of the acetyl group having occurred during methylation. From the product, after de-acetylation, alizarin β methyl ether was precipitated from an alcoholic solution as the potassium salt by means of potassium hydroxide, the α-methyl ether remaining in solution. *Acetylalizarin α-methyl ether* forms yellow needles, m p. 212°;

Anthragallol 1 *2-dimethyl ether* (I), yellow needles, m.p. 230°–232°, and *anthragallol* 1 3-*dimethyl ether* (II), yellow needles, m p 218°–220°.

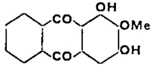


I.

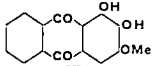


II.

The former is distinguished from the latter in that it forms a red ammonium salt soluble in cold alcohol, whereas the ammonium salt of the 1:3-dimethyl ether crystallises in scarlet prisms which are sparingly soluble in cold alcohol. Both ethers are readily converted by methyl sulphate into the trimethyl ether, and when heated with 10% potassium hydroxide solution at 180° for 5 hours, the 1.2 dimethyl ether is partially converted into methoxypurpuroxanthin (III), and the 1:3-dimethyl ether into methoxyalizarin (IV):



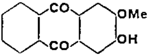
III.



IV.

The constitutions (I and II) assigned to these anthragallol dimethyl ethers by Perkin and Hummel (*l c.*) have been confirmed by synthesis (Perkin and Story, J.C.S. 1929, 1399). Partial acetylation of anthragallol 2-methyl ether yields 3-acetylanthragallol 2 methyl ether which, by the action of diazomethane, is converted into a mixture of anthragallol trimethyl ether and 3-acetylanthragallol 1:2 dimethyl ether The latter, when hydrolysed, gives anthragallol 1 2-dimethyl ether identical with the natural product. The 1:3-dimethyl ether is obtained by partial benzoylation of anthragallol 3 methyl ether and treatment of the resulting 2 benzoylanthragallol 3-methyl ether with diazomethane, which gives not only 2-benzoylanthragallol 1 3 dimethyl ether (16%), but also 1-benzoylanthragallol 2 3-dimethyl ether (80% approx), the benzoyl group having thus migrated from the 2- to the 1-position. Hydrolysis of the former compound gives anthragallol 1 3-dimethyl ether identical with that present in chay root;

Hystazarin Monomethyl Ether,



long orange-yellow needles, m p. 232°, dissolves in alkaline solutions with a crimson coloration, and its ammonium and potassium salts, which crystallise in garnet red needles, are insoluble in cold isobutyl alcohol. When heated with hydrochloric acid at 180° it is converted into hystazarin, whilst methylation with methyl sulphate affords *hystazarin dimethyl ether*, yellow glistening needles, melting at 235°–236°,

β Hydroxyanthraquinone, pale yellow needles, m p. 302°. This is identical with the synthetic product prepared from anthraquinone β sulphonic acid by digestion with alkali.

Dyeing Properties.—Chay root contains acid principles which tend to dissolve the mordants, and it is thus necessary to add 2% of chalk to the dyebath and to raise the temperature gradually to the boiling point.

Dyeing experiments on calico, stripe printed with aluminium and iron mordants, have shown that the dyeing power of chay root is equivalent to the presence of 0 33–0·35% alizarin. The reds, pinks, and chocolates have a distinctly bluer shade than those given by madder, and the lilacs are much fuller and brighter and very similar to those obtained from alizarin. On oil-prepared calico, mordanted with alumina, chay root gives an excellent blue shade of Turkey-red, whilst brown, red, orange and purple colours are obtained on wool or silk mordanted with chromium, aluminium, tin or iron respectively.

Boiled with dilute sulphuric acid, chay root yields a "garancine" of a very dark green colour and possessing about three times the dyeing power of the original root.

A. G. P. and E. J. C.

CHAYOTE. The fruit of *Sechium edule* Swartz (or *Chayota edulis* Jacq.) a member of the gourd family. The chayote is a native of Central and Southern America, and is cultivated in many tropical and sub tropical areas. The large pear-shaped single seeded fruit, which may weigh from 0 4–2 5 kg, is a valuable starchy food and the young leaves, tips and shoots also serve as green vegetables. According to Valenzuela and Waster (Philippine J. Sci.

1930, 41, 85) the composition of the chayote is : H_2O 93·3, protein 0·64, fat ·024, N-free extract 5·25, fibre 0·4, ash 0·23%. The nitrogen bases include arginine and guanidine with small proportions of adenine and choline. A. G. Po.

CHEDDITES. These chlorate explosives were patented by Street (B.P. 9970) in 1897, the name being derived from Chedde, the town in France where they were first prepared.

Composition.—A number of varieties have been manufactured, but essentially they consist of a chlorate, usually the potassium salt, a fatty oil such as castor oil, together with one or more nitro aromatic compounds such as mononitronaphthalene, dinitrobenzene, dinitrotoluene, etc.

The early attempts to substitute the cheaper sodium chlorate for the potassium salts were not very successful as the mixtures were found to be too insensitive to detonation, even when moderately compressed. It was found, however, that a sodium chlorate mixture containing 16% of dinitrotoluene and no other nitro body formed an explosive which was more powerful than the older types and it could be fired at densities up to 1·65.

The compositon of some of the more important cheddites is given in the following table :

Type.	O1 Type 41. %	O1 Type 60 bis. %	O2 Type 60 bis M. %	O5 %
Potassium chlorate	80	80	79	—
Sodium chlorate	—	—	—	79
Castor oil	8	5	5	5
Mononitronaphthalene	12	13	1	—
Dinitrotoluene	—	2	15	16

The French cheddites are coloured with different oil-soluble dyes in order that the various types can be easily distinguished from one another by visual examination alone.

Gelatinised cheddites containing nitrocellulose have also been manufactured, the following being a typical composition : sodium chlorate 75%, dinitrotoluene (liquid) 23·75%, nitrocellulose 1·25%. A further variety contains nitroglycerin in addition to nitrocellulose, the composition being: sodium chlorate 70%, dinitrotoluene (liquid) 23·5%, nitrocellulose 1·5%, and nitroglycerin 5%.

Manufacture (*non-gelatinised type*).—The nitro compounds are dissolved in the castor oil by heating the mixture in a steam-jacketed enamelled iron pan at a temperature of 70°–80°C. When the mass is homogeneous it is allowed to cool to 55°C., when the warm, dry, and finely powdered chlorate is mixed in by means of a wooden spatula, care being taken to ensure that each particle of chlorate is coated with the oily mixture. The mass is poured on to a wooden bench, allowed to cool to about 30°–35°C., and then crushed by means of a wooden roller. After sifting to remove fine particles, the explosive is made into cartridges by pressing into wooden moulds from which it is transferred to paper cases. The cartridges containing sodium chlorate cheddites should be dipped in molten paraffin wax in order to prevent the adsorption of moisture.

Gelatinised Cheddites.—In the manufacture of this type of the explosive, the nitrobodies are mixed with the nitrocellulose and nitroglycerin and gelatinised at a temperature of about 40°C., the chlorate being incorporated afterwards. This form of cheddite is made into cartridges by a machine similar to that used for ordinary gelatinised explosives.

Properties.—The non-gelatinised cheddites are in the form of soft white or yellowish grains unless they have been artificially coloured. They are readily compressible and in order to obtain the full explosive power it is necessary to carefully control the density. If the density is low, the maximum power is not developed, whereas very high compression leads to difficulty in detonation. The non-gelatinised cheddites are relatively insensitive to shock and friction at ordinary temperatures and burn more or less rapidly without any tendency to explode, even when fired in large masses. Heating at 120°C. for an appreciable period causes no decomposition, but at 200°C. the oil decomposes, the nitrocompounds volatilise, and the explosive darkens. Small quantities when heated deflagrate at about 250°–260°C.

According to Will (Z. ges Schiess- u. Sprengstoffw. 1906, 1, 209), a 2 kg. weight falling 32 cm. causes explosion of cheddite 60, whereas for cheddite 41, a fall of 36 cm. is required.

The velocity of detonation increases with the density up to a certain point, but beyond that diminishes rapidly. According to Dautriche, cheddite 60 bis O1 in cartridges having a diameter of 40 mm. and a density of 0·7 gave a velocity of 2,283 m. per sec., whereas at a density of 1·17 the velocity was 2,901 m. per sec. At a density of 1·4 the velocity was reduced to 2,451 m. per sec., and at 1·5 the explosive failed to detonate.

Explosive Power.—When detonated in the Trauzl block, cheddites give expansions varying from about 250 to 400 ml., depending upon the variety of the explosive used. Owing to the relatively low rate of detonation their violence as measured by the copper cylinder crushing test is less than half that shown by blasting gelatine under the same conditions.

According to Brevetta (Z. ges Schiess- u. Sprengstoffw. 1906, 1, 125), types No. 60 and 60 bis have an explosive power of at least double that of black powder and equal to Dynamite No. 1 H. S.

CHEESA STICKS. Lengths of cordite coated with ammonium oxalate and shellac. They are used in South Africa as fuzes for blasting charges. H. S.

CHEESE. A solid preparation of the chief constituents of milk, consisting mainly of coagulated casein (*q.v.*), fat, water, and some mineral matter.

The modified protein thrown out of milk by the action of rennet is designated " paracasein," a substance which produces an insoluble compound with calcium (Associates of L. A. Rogers, " Fundamentals of Dairy Science," 1928, p. 202 *et seq.*).

Cheese is, however, a very different product from the " curd," which is only the first step in its production. The proteolytic enzymes of the rennet continue to act in the curd; bacteria

present in the original milk and added in the form of "Starter" contribute to the flavour of the cheese. Moisture controlled by cutting, draining, milling, and pressing the curd and by the temperature and acidity at which these operations are conducted determines "body" and "texture" of the final product (J. G. Davis, J.S.C.I. 1935, 54, 27, 631).

Cheese may be made from the milk of various animals, but cow's milk as a rule provides the raw material. It is either used in its natural condition or may be pasteurised or separated, cheese being sometimes made from cream (cream cheese), and also from skimmed or partly separated milk. The use of rennet is sometimes omitted in the case of "cream" and "cottage" cheese.

Coloured cheeses, e.g. Leicester and Dutch, owe their colour to annato, added to the milk some 10 minutes before renneting.

Different varieties of cheese owe their peculiarities to differences in the technique of manufacture developed in localities from which their names are derived, though it is probable that a process of selection has resulted in the choice of a method of manufacture best suited to type of milk, flora (bacterial and plant), soil, and atmospheric conditions of the locality. In so far as these conditions are understood geographical limitations to the manufacture of cheese vanish.

Cheddar, Cheshire, Derby, and Leicester are hard pressed cheeses; the pressure on the cheese in the mould is regulated in the cheese press and may finally exceed 2 tons per cheese. In the case of Stilton, Roquefort, and Gorgonzola the pressure in the mould is greatly reduced or omitted.

About half the constituents of the milk appear in the cheese, the remainder is run off in the liquid "whey" which contains the sugar, albumin, and salts together with a little fat. The value of this by product is now being realised since improved and more economical methods of driving off the water have been invented.

The increase in the coagulation time with rennin observed in "flash" pasteurised milk is associated with a decrease in the whey nitrogen (Moir, J. Dairy Res. 1930, 2, 68; 1931, 3, 80). The use of pasteurised milk for cheese making is gaining ground. Hydrochloric acid is sometimes used to accelerate coagulation.

Methods for the sampling and analysis of cheese have been drawn up (Int. Rev. Agric. 1934, 25, 3, 111). Samples are taken with a cheese borer of a sufficient length to take cores from the flat end of a cheese at least half way through. Alternatively wedge shaped slices may be cut; 1 to 2 cm. of the rind is removed and a representative sample of at least 40 g. is enclosed in a sealed vessel and examined without delay.

Samples may be tested for fat by the Gerber method, a special butyrometer being used for the determination, the basis of graduation is that 1·350 ml. correspond to 10% fat, 3 g. of cheese shavings being weighed into a special weighing funnel for the test (British Standards Specification 1936, No. 696, Part I, p. 23). A Gerber milk butyrometer may be used instead, taking about 1 g. for the test, a table for calculation published in B.S.S. 1936, No. 696, Part 2, p. 27 is required in this case.

For the more exact chemical analysis of the percentage of fat in cheese, 3 g. of cheese is heated with 10 ml. of hydrochloric acid (sp. gr. 1·125), after the curd is dissolved 10 ml. of alcohol (96%), 25 ml. ethyl ether, and 25 ml. light petroleum (b.p. 40°–60°C.) are added, shaking in a stoppered tube after each addition. After standing for 2 hours, or spinning in a centrifugal machine, the ethereal solution of fat is transferred to a weighed flask and after two further successive extractions with the two mixed solvents the solvents are evaporated and the fat dried at 102°C.

The moisture is determined on 3 g. or alternatively 5 g. of cheese, weighed into a flat dish, and mixed and spread with the flattened end of a glass rod which should be weighed with the dish; after preliminary drying in air or *in vacuo*, drying is finished till constant in an oven at 100°–105°C.

The salt may be determined in 2 g. of the original cheese weighed into a conical flask, and taken up with 10 ml. of distilled water; 25 ml. of 0·05*N*-silver nitrate is added and after warming and mixing with 10 ml. conc. nitric acid, the heating is continued until the curd is digested; 2 ml. of a saturated solution of iron alum in 10% nitric acid is added and the volume made up to 100 ml. The excess silver nitrate is titrated with 0·05*N*-potassium thiocyanate until an orange tint persists for 15 seconds. Standardised by the Volhard method against sodium chloride of known strength, 1 ml. 0·05*N*-thiocyanate=0·00292 g. sodium chloride.

The titratable acidity calculated as lactic acid per 100 g. of cheese is determined on 2 g. of cheese weighed into a small porcelain mortar (in the case of hard cheese), or a 250 ml. conical flask in the case of soft cheese), ground into a fine paste with 10 ml. water diluted and titrated with 0·1*N*-sodium hydroxide using phenol phthalein as an indicator.

The total nitrogen may be determined by the Kjeldahl method, but this figure ×6·39 only gives a rough indication of the original proteins in the unripened cheese as the protein is broken down during ripening with loss of nitrogen.

J. G.

The Microbiology of Cheese.

The role of micro organisms in cheese ripening is complex and still imperfectly understood. There is, however, a well defined difference between the mould ripened and the "hard" (Cheddar) type of cheese.

The progress of events in the latter is briefly as follows. The common organisms of ordinary milk, including the ubiquitous coliform types together with certain streptococci, attack the proteins to a slight extent and provide a suitable nitrogenous substrate for the lactic acid bacteria which are added in the form of "starter." The starter contains streptococci of the *Str. lactis* or *Str. cremoris* types, and many also contain *Str. paracitrovorus*. Starters may be pure cultures or mixed cultures of pure strains. These organisms rapidly proliferate in

milk and their first function is to develop that acidity which is most favourable to rennet action. During their rapid growth the so-called "miscellaneous flora" is suppressed although as a rule by no means destroyed. After coagulation by rennet and the cutting of the curd, acidity continues to increase during piling or "cheddaring" until the p_H of the curd reaches about 4·8. The addition of salt imposes a temporary check to growth of the streptococci, but within about 2 days most of the lactose remaining in the curd is fermented. No lactose can be detected after 7 days. The acid condition of the "green" cheese prevents the growth of organisms which may break down the proteins with the formation of unpleasant compounds. The streptococci are replaced after about 14–30 days by lactobacilli. In Cheddar cheese these are of the *Lactobacillus casei* and *Lactobacillus plantarum* types. These organisms are characterised by their ability to grow under acid conditions and are good examples of the so-called "aciduric" organisms. It appears that the lactobacilli are responsible for the production of flavour in cheese, since if protein-splitting enzymes are allowed to act on milk solids in the presence of chloroform no flavour is produced although scission to lower compounds is well marked. While a certain amount of protein breakdown is accomplished by the lactic acid flora, this action is mainly due to rennet enzymes. The flavour appears to be due to the formation of volatile acids and their esters and other derivatives.

Although the flora of the English hard pressed cheese is mainly *Str. lactis, Str. cremoris, Lactobacillus casei*, and *Lactobacillus plantarum*, other types are present. Thus a variety of micrococci which are aciduric may usually be found in some numbers and it is possible that they contribute to the ripening process. *Str. liquefaciens*, a proteolytic type of acid-forming organism, may usually be recovered from ripening cheese.

In cheese which has been incorrectly made and in which insufficient acid has been allowed to develop during making, as, for example, when the starter fails, putrefactive anaerobic organisms derived from dirt or from unsuitable rennet may proliferate and produce vile-smelling compounds rendering the cheese quite unfit for consumption. The p_H of such cheese is invariably much higher than that of the normal (p_H=5·4) ripe Cheddar cheese.

Other faults may be due to the growth of coliform organisms which produce gas and unpalatable products of fermentation. One lactic acid organism, *Lactobacillus rudensis*, produces a brick red pigment within the cheese.

The mould-ripened cheeses (Stilton) owe their special characters to a combination of bacterial and mould ripening. In the early stages much the same processes as in hard cheese occur. The lactose of the milk and of the curd after coagulation is fermented by streptococci. Since more moisture is retained in the Stilton curd the process of acid formation continues after the curd is put into moulds. After some two months of ripening, first by streptococci, then by lactobacilli, moulds make their appearance within the cheese. Their growth is made possible by the opening up of cracks, because of the loss of moisture by evaporation and also because of the looser texture of the curd (little or no pressure is used in manufacture). These moulds of the *Penicillium roquefortii* type which will grow in low tensions of oxygen, cause profound breakdown of the partially ripened curd with the production of quantities of ammonia, remove the volatile fatty acids produced earlier and replace them by volatile acids higher in the series. Considerable quantities of capric and caprylic acids, to which the flavour is ascribed, make their appearance.

A. T. R. M.

CHEIRANTHIN *v.* CHEIRANTHUS CHEIRI L.

CHEIRANTHUS CHEIRI L., the wall-flower, contains in its seeds 1·6–1·7% of a neutral substance *cheirolin*,

$$CH_3{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NCS\ ;$$

this forms colourless prisms, m.p. 47°–48°C., and has been synthesised by Schneider (Annalen, 1910, **375**, 207). It is unique as a naturally occurring sulphone and is evidently derived from the amino-acid methionine,

$$CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2)COOH,$$

present in many proteins (*cf.* Barger and Coyne, Biochem. J. 1928, **22**, 1417). Cheirolin is present as a sinigrin-like glucoside, which is hydrolysed by myrosin from white mustard seeds. Wall-flower seeds contain an enzyme capable of liberating mustard oil from (myrosin-free) black mustard seeds (Schneider and Lohmann, Ber. 1912, **45**, 2954). Cheirolin has been stated to be antipyretic (Wagner, Chem.-Ztg. 1908, **32**, 76) and to be not identical with *cheirinine*, $C_{18}H_{35}O_{17}N_3$ (?), a substance isolated from wall-flower leaves by Reeb (Arch. exp. Path. Pharm. 1898, **41**, 302 ; 1899, **43**, 130) and somewhat resembling quinine in pharmacological action. Reeb also obtained a S-free glucoside, *cheiranthin*, which according to Jaretzky and Wilcke (Arch. Pharm. 1932, **270**, 81) has a minimal lethal dose of $2{\cdot}2\times10^{-7}$ g. per g. of frog, and is more active than the digitalis glucosides ; it is present in the seeds and to a less extent in the leaves. Cheirolin and cheiranthin also occur in the seeds and leaves of the related genus *Erysimum*.

G. B.

CHEIRININE *v.* CHEIRANTHUS CHEIRI L.

CHEIROLIN *v.* CHEIRANTHUS CHEIRI L.

CHELERYTHRINE *v.* CHELIDONIUM MAJUS, ALKALOIDS OF.

CHELIDONINE *v.* CHELIDONIUM MAJUS, ALKALOIDS OF.

CHELIDONIUM MAJUS, ALKALOIDS OF. Eleven alkaloids have been isolated from *C. majus*; the six important bases may be separated into three groups, of which each second member differs from the first by having two methoxyl instead of one methylene-dioxy-group, viz.:

chelidonine → homochelidonine,
sanguinarine → chelerythrine,
protopine → α and β-allocryptopine.

Further alkaloids isolated from commercial residues were oxychelidonine, methoxychelidonine,

a base $C_{19}H_{21}ON_2$, and sparteine Most of the chelidonium alkaloids do not only occur in *C. majus* but are somewhat widely distributed in the Fam. Papaveraceæ, such as:

Sanguinaria canadensis (blood-root), containing chelerythrine, α allo-cryptopine, β allo-cryptopine, sanguinarine.

Glaucium luteum: chelerythrine, sanguinarine (uncertain), and protopine.

Eschscholzia californica: chelerythrine and sanguinarine (uncertain).

Bocconia cordata: chelerythrine, α- and β-allo-cryptopine, sanguinarine (uncertain), and protopine.

Stylophorum diphyllum: chelidonine, sanguinarine.

Adlumia cirrhosa: allo-cryptopine.

Zanthoxylum brachyacanthum (Fam. Rutaceæ). β allo-cryptopine, α and β allo cryptopine.

Preparation of the Alkaloids.—The dried roots are exhausted with EtOH containing acetic acid. The residue after distilling off EtOH is basified with NH_3 and extracted with $CHCl_3$ The residue after evaporating the solvent is treated with cold dilute alcoholic HCl, when protopine and chelidonine hydrochlorides remain undissolved. Excess of ammonia is added to the filtrate when chelerythrine and homochelidonine are precipitated; α allo cryptopine may be obtained by extracting the mother liquor with $CHCl_3$.

The starting material for the investigation of the chelidonium bases was usually crude commercial residues devoid of chelidonine. The separation and purification of most of these alkaloids is difficult, Gadamer and Stichel (Arch Pharm 1924, 262, 488) separate the quaternary bases sanguinarine and chelerythrine from other alkaloids through the pseudo cyanides (*cf.* Karrer, Ber 1917, 50, 212) Chelerythrine and sanguinarine may be separated through the tartrates (Gadamer and Stichel, *l c*) or by fractionating the two pseudo cyanides with acetone (Späth and Kuffner, Ber. 1931, 64, 1123) Another interesting way for preparation of chelerythrine from *Sanguinaria canadensis* was reported by Bauer and Hedinger (Arch Pharm. 1920, 258, 168) The yield of total crude alkaloids in the latter case was. 0 66, 0 77, 1 62, and 1 74% respectively.

Chelidonine (I), $C_{20}H_{19}O_5N,H_2O$, $[\alpha]_D$ +115 4° (in EtOH), m p. 135°–136° (anhydrous), crystallises in monoclinic tablets and distils as colourless oil at 220°/0 002 mm. It is best freed from protopine (*v supra*) by purification with Et_2O, in which (I) is less soluble; the free base may be recrystallised from acetic acid, EtOH, or from EtOH–$CHCl_3$ (I) is readily soluble in EtOH or Et_2O, insoluble in H_2O. B HCl, B HNO_3, and B HI are colourless and crystalline, the nitrate is sparingly soluble in H_2O, more soluble in EtOH. For absorption spectrum of (I), *see* Brustier (1930, A, 626).

(I) contains a secondary alcoholic OH-group; *monoacetyl* (I), $[\alpha]_D$ +110°, m p. 165°–168° (m p 184°–186 , *cf.* Gadamer and Winterfeld, Arch. Pharm. 1924, 262, 470) is obtained by treating (I) with cold acetic anhydride; it crystallises from MeOH. *N-acetyl-anhydro*-(I), optically inactive, m p 152° (from $CHCl_3$–EtOH) by treating (I) with hot acetic anhydride and Na-acetate (Gadamer and Dieterle, *ibid* 1924, 262, 265). (I)-methine A, $[\alpha]_D$ −271 3° (in $CHCl_3$), m.p. 145°–146° from ether, and (I) methine B, $[\alpha]_D$ −100° (Gadamer, 1924, 262, 257).

Homochelidonine (II) (called α homochelidonine in earlier papers), $C_{21}H_{23}O_5N$, dextrorotatory, m p. 182° (from $CH_3{\cdot}CO_2Et$), readily soluble in $CHCl_3$, less so in $CH_3{\cdot}CO_2Et$ and EtOH sparingly soluble in Et_2O. It occurs in commercial chelidonine residues in an amount of about 6% (Selle, Arch. Pharm. 1890, 228, 450) B HCl, very soluble in H_2O, apparently amorphous; B-aurichloride, crystalline; B platinichloride, amorphous. (II) contains two methoxyl groups, one methylenedioxy- and a secondary alcoholic OH-group.

Sanguinarine (III), $C_{20}H_{15}O_4N$ OH, colourless, quaternary optically inactive base, crystallising with 1 mol. of EtOH or H_2O, melts anhydrous at 242°–243° (decomp) or at 195°–197° (recrystallised from solvents containing EtOH). (III)-pseudo-cyanide is a non-basic colourless substance, soluble in Et_2O, crystallises from $CHCl_3$–EtOH, m p. 238°. The hydrochloride may be recovered by boiling the pseudo cyanide with strong HCl. (III) yields very characteristic copper red salts (III) is best prepared from commercial "chelidonine residues" (Gadamer and Stichel, *ibid* 1924, 262, 488) or by extraction of *Sanguinaria canadensis* (Schmidt, Koenig and Tietz, *ibid* 1893, 231, 145).

Earlier reports concerning (III) should be read with caution, as apparently the investigators often handled a mixture of (III) and chelerythrine For separation, *see* Gadamer and Stichel (*l c*), Späth and Kuffner (*l c*) (III) contains two methylene dioxy groups Gadamer and Winterfeld (*l c*) by oxidising O acetyl-(I) with mercuric acetate obtained (III), which at that time was called pseudo chelerythrine (*cf also* von Bruchhausen and Bersch, Ber 1930, 63, (B), 2524).

Chelerythrine (IV), $C_{21}H_{15}O_4N$ OH, colourless, optically inactive quaternary base, m p. 207° (from EtOH or CH_3 CO_2Et) crystallises with 1 mol of EtOH. (IV) is readily soluble in $CHCl_3$ or benzene, less in EtOH, Et_2O, acetone, or MeOH The alcoholic solution of pure (IV) is colourless and non-fluorescent (IV)-pseudo-cyanide is a non-basic substance soluble in Et_2O, m.p 260°–261°. The salts of (IV) are intensely yellow: B Cl+H_2O, citron yellow needles; B_2 SO_4, golden yellow needles, sparingly soluble in H_2O, the platinichloride and aurichloride are also crystalline

The best source of (IV) is *Sanguinaria canadensis* (*cf* Bauer and Hedinger, *l c.*) For separation of (IV) and (III), *see* Späth and Kuffner, (*l c*) There is the same relation between (IV) and (II) as between (III) and (I) by oxidation of O acetyl (II) with mercuric acetate (IV) is obtained (Gadamer, Arch Pharm 1920, 258, 160)

*a-allo*Cryptopine (V) (called *β*-homochelidonine in earlier papers), $C_{21}H_{23}O_5N$, optically inactive, crystallises in monoclinic prisms, m.p. 159°–160° (from $CH_3 \cdot CO_2Et$), sparingly soluble in EtOH and benzene, easily soluble in $CHCl_3$. B·HCL+$1\frac{1}{2}H_2O$, needles, easily soluble in H_2O; B·HNO_3+$1\frac{1}{2}H_2O$, sparingly soluble in H_2O; also B·HBr and B·HI are crystalline. Methiodide, m.p. 185°.

The behaviour of (V) is very similar to cryptopine (*q.v.*); Gadamer (Arch. Pharm. 1920, 258, 148) by interaction of $POCl_3$ and (V) obtained *iso-allo*cryptopinechloride identical with dihydro-anhydro-berberinemethochloride. (V) therefore has a ten-membered ring-system like cryptopine with a methylenedioxy-group in 2-3-position and two methoxyl-groups in position 9 and 10.

*β-allo*Cryptopine (VI) (called *γ*-homochelidonine in earlier papers), m.p. 169°, crystallises in large, colourless tablets. It is a physical isomeride of (V), crystallises with the latter, and can be mechanically separated from the small prisms of (V).

Oxychelidonine (VII), $C_{20}H_{17}O_6N$, $[\alpha]_D$ +102·5°, m.p. above 285°, crystallises from $CHCl_3$–EtOH in pointed needles. (VII) is a non-basic substance probably containing two methylenedioxy-groups. The constitution is still unknown, for further details, *see* Gadamer and Theissen (Arch. Pharm. 1924, 262, 578).

Methoxychelidonine (VIII), $C_{21}H_{21}O_6N$, $[\alpha]_D$ +115° 48′, m.p. 221°, colourless prismatic crystals from EtOH, sparingly soluble in Et_2O, easily soluble in EtOH and $CHCl_3$. (VIII) contains —NMe, —OMe, and two methylenedioxy-groups. The constitution is still unknown. For colour-reactions and further details, *see* Gadamer and Winterfeld (Arch. Pharm. 1924, 262, 589).

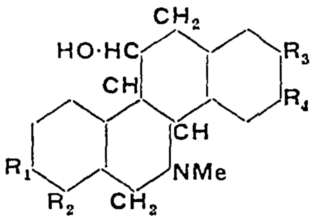
Base, $C_{19}H_{24}ON_2$, $[\alpha]_D$ −40° 42′, m.p. 198°–199°, colourless needles, easily soluble in EtOH and $CHCl_3$, less in Et_2O. The alkaloid is dibasic, for further details *see* Gadamer and Winterfeld (*l.c.*, 1924).

Sparteine has been isolated from commercial "chelidonine residues" (*cf.* Späth and Kuffner, Ber. 1931, 64, [B], 1127).

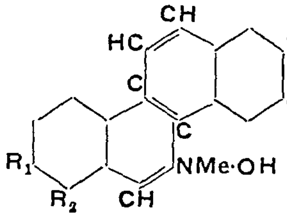
Constitution of (I)–(IV).—As a result of a large number of investigations, the structures of the four alkaloids have recently been established (I)–(IV) are derivatives of naphthophenanthridine, a ring-skeleton not hitherto known in alkaloid chemistry.

F. von Bruchhausen and Bersch (Ber. 1930, 63, 2520; 1931, 64, 947) obtained hydrastic acid and 2(dimethylaminomethyl)-3:4-methylenedioxybenzoic acid by oxidation of (I), and from these results proposed formula A for (I) and B for (III) $\left(R_1+R_2 \text{ and } R_3+R_4=CH_2\langle{}^{O-}_{O-}\right)$. Späth and Kuffner (Ber. 1931, 64, [B], 370) obtained trimellitic acid (benzene-1:2:4-tricarboxylic acid) by oxidation of *N*-acetyl-anhydrochelidonine with nitric acid, and hydrastic and *iso*hydrastic acid (the latter corresponding to von Bruchhausen's basic degradation products) by *oxidation of* (I) with permanganate. These authors also obtained α-naphthophenanthridine by zinc-dust distillation of (III) and (IV). By oxidation of (IV) Späth and Kuffner (*ibid.*) 1123 obtained *m*-hemipinic acid and hydrastic acid, they attribute to (II) formula A and to (IV) formula B $\left(R_1 \text{ and } R_2=OMe;\ R_3+R_4=CH_2\langle{}^{O-}_{O-}\right)$.

For a further proof of the relationship of (II) and (IV), *see* Späth and Kuffner (Ber. 1931, 64 2034).



A.



B.

Physiological Action of Chelidonium Alkaloids.—(IV) is poisonous, it paralyses the central nervous system without any increase in irritability, resembles protopine in its muscular action, and first irritates and then paralyses the sensory nerve terminations (Henry, "Plant Alkaloids," 2nd ed., p. 253).

(I) and (II) are only slightly toxic, (I) resembles papaverine in its action and could be used as an antispasmodic. The pharmacological action of (I) was studied in greater detail by Hanzlik (Zentr. Physiol. 1914, 28, 551; J. Pharm. Exp. Ther. 1915, 7, 99; J. Amer. Med. Assoc. 1920, 75, 1324; J. Pharm. Exp. Ther. 1921, 18, 63; 1928, 33, 387).

None of the chelidonium alkaloids are used as such in medicine; tincture of sanguinaria is no longer included in the "United States Pharmacopœia." Schl.

"CHELLAK" *v.* CHELLOLGLYCOSIDE.

CHELLOL *v.* CHELLOLGLYCOSIDE.

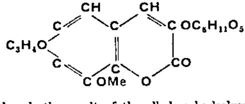
CHELLOLGLYCOSIDE,

$C_{19}H_{20}O_{10}2Aq.$,

m.p. 175°, $[\alpha]_D$ −31·9°, is present in the seeds of *Ammi Visnaga*, an umbelliferous plant common in the Nile Delta and termed "chellak" by the natives (Fantl and Salem, Biochem. Z. 1930, 226, 166).

Acid hydrolysis yields glucose and an aglucone, *chellol*, $C_{13}H_{10}O_5$. *Alkaline hydrolysis* yields *d*-glucosido-glycollic acid (Fischer and Helferich, Annalen, 1911, 383, 83) and a product, $C_{11}H_{10}O_4$,

which contains an α pyrone ring. The glycoside is provisionally formulated as



although the result of the alkaline hydrolysis indicates that glycollic acid is the middle unit of the molecule E. F. A

CHEMAWINITE v. AMBER or SUCCINITE.

CHEMICAL AFFINITY. From the early period, when the study of chemistry was beginning to develop into a science, the causes that determine the direction and velocity of a chemical reaction have always excited interest The term *chemical affinity* arose from the attempt to find some scale by which the tendency of compounds to react could be measured. Tables were compiled in which related substances were arranged in the order in which they would replace one another from their compounds Bergman in 1775 published such a list, which became known as an "affinity table," although the same idea had been put forward by St F. Geoffroy as early as 1718 Such attempts at classification invariably broke down when more than a few elements were considered Equally unsuccessful was the suggestion by Wenzel (1777) that the actual velocity was a measure of affinity. Finally Thomson approached the problem *in terms of the heat evolved from the reaction*, which later led to the satisfactory representation of the energy changes involved in terms of the Gibbs Helmholtz equation. But neither thermodynamics nor the applications of modern theoretical physics as yet enable us to prophecy the kinetics of a reaction (*see* "Thermodynamics of Chemical Equilibrium and Reaction Rates," M G. Evans and M Polanyi, Trans. Faraday Soc 1936, 32, 1333) On the other hand, increasingly careful quantitative work has been carried out on the influence of concentration, temperature, pressure, and the presence of foreign substances on the course and products of reactions The object of this article is to give an outline of the methods employed and the results obtained in this study

Velocity of Chemical Reactions.

The rate of a chemical change depends on the nature of the reactions and the temperature at which it is taking place At a suitable temperature, conditions can be found for all reactions in which the velocity can be measured in the laboratory. The reaction, proceeding in a homogeneous phase, can be represented generally as $A+B+\text{etc}=C+D+\text{etc}$ Assuming that finally A and B are completely transformed into C and D, the problem is to determine the connection between the concentrations of A and B and the velocity of their transformation into B and C.

In a homogeneous system the problem can be approached from the molecular kinetic theory. A and B can only react when their molecules come into collision and even then only a certain *percentage of those collisions* will lead to combination. Hence the rate of disappearance of A and B will be proportional to the number of collisions between them, and this is proportional to the product of their concentrations.

The foregoing argument may be expressed mathematically. If a is the concentration of a substance A, and b is the concentration of a substance B at the beginning of the reaction, then the initial velocity V_0 of the change is given by the equation $V_0=k_1ab$, where k_1 is a proportionality factor, the numerical value of which is independent of the concentrations of the reacting substances, and varies only with temperature and other external conditions If the reaction is allowed to proceed for an interval of time t, and if x represents the extent to which the concentrations of A and B have been diminished by the progress of the change, then the velocity V_t at time t is given by the equation $V_t=k_1(a-x)(b-x)$. It is obvious that V_t must be less than V_0, and that the velocity of the reaction must diminish continuously from the start onwards: V_t therefore represents the velocity of the reaction only for an infinitely short space of time. This velocity is defined by the rate at which x is, at that moment, increasing with the time, and if, using the language of the differential calculus, we indicate by dx the extent to which x increases in the infinitely short space of time dt, we may write $V_t=\frac{dx}{dt}=k_1(a-x)(b-x)$.

The applicability of the law of mass action, as expressed in the foregoing formula, is best appreciated by reference to a particular case, such as the inversion of sucrose. Although this change, which may be represented by the equation $C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$, takes place with appreciable velocity only in the presence of a catalytic agent such as hydrochloric acid, yet the latter is found unaltered when the reaction is over, and the inversion of sucrose may be regarded as a particular case of the reaction $A+B=C+D$. The fact that the *inversion is carried out in aqueous solution* permits a simplification of the formula

$$\frac{dx}{dt}=k_1(a-x)(b-x)\ ;$$

the water taking part in the reaction is a small fraction of the total water present, so that x may be neglected in comparison with b, and we may write $\frac{dx}{dt}=k(a-x)$, where $k=k_1b$. Integration of this equation leads to the formula $k=\frac{1}{t}\log_e\frac{a}{a-x}$, in which, as already indicated, a is the initial concentration of sucrose, and $a-x$ is its concentration after the inversion has proceeded for t units of time.

The above is the general formula for a reaction where one molecular species is changing in concentration—a unimolecular or first order reaction. To test the formula it is only necessary to follow the change in concentration of sucrose with time by observing the change in

the angle of rotation of polarised light in a polarimeter. The test solution must, of course, meanwhile be kept at constant temperature by a suitable water jacket.

The angle of rotation is determined at the beginning of the change, at subsequent intervals, and finally when the change is complete. If we indicate by θ_0, θ, and θ_a the initial angle of rotation, the angle at a time t from the start, and the final angle respectively, then $\theta_0-\theta_a$ is a measure of a, the total sucrose undergoing inversion ; and $\theta-\theta_a$ is similarly a measure of $a-x$, the sucrose which has still to undergo inversion after time t. Hence $\frac{a}{a-x}=\frac{\theta_0-\theta_a}{\theta-\theta_a}$; and the formula which should represent the course of the inversion becomes $k=\frac{1}{t}\log_e\frac{\theta_0-\theta_a}{\theta-\theta_a}$. From the ascertained values of t, θ_0, θ and θ_a, it is easy to discover whether the expression on the right-hand side of the equation is constant or not. The experimental data recorded in the following table show how far in a particular case the actual course of sucrose inversion corresponds with the velocity formula :

INVERSION OF SUCROSE AT 25° BY $N/2$-HCl.

t in minutes.	θ angle of rotation.	$k=\frac{1}{t}\log_{10}\frac{\theta_0-\theta_a}{\theta-\theta_a}$
0	25·16°	—
56	16·95°	0·00218
116	10·38°	0·00218
176	5·46°	0·00219
236	1·85°	0·00219
271	−3·28°	0·00221
indefinite	−8·38°	—

The expression evaluated in the last column is $\frac{1}{t}\log_{10}\frac{\theta_0-\theta_a}{\theta-\theta_a}$ instead of $\frac{1}{t}\log_e\frac{\theta_0-\theta_a}{\theta-\theta_a}$, but, obviously, if the value of the *former expression* is constant, the value of the latter must be so also. The figures in the last column are satisfactorily constant, and the figure 0·00219 may therefore be taken as the velocity coefficient for the inversion of sucrose under the specified conditions, viz. at 25° and in presence of $N/2$-HCl.

Two characteristics of unimolecular reactions which are implicit in the formula deserve emphasis. First, for all unimolecular processes the amount of change occurring in a given time is a constant fraction of the unchanged material still present. This follows from the fundamental equation and is obvious when it is written in the form $\frac{dx}{a-x}=kdt$. It shows that the numerical value of k is unaltered whatever concentration terms are chosen to represent x ; a point where unimolecular changes differ from those of higher order. The second feature is that the amount of material transformed in a given time is always the same fraction of the substance present at the beginning of the period considered, however widely this be varied.

Innumerable examples of reactions that quantitatively follow a unimolecular course are known ; but the majority of them resemble the inversion of sucrose in that although the first order equation is followed, more than one molecule enters into the change, which is consequently only pseudo-monomolecular. Indeed, before the decomposition of nitrogen pentoxide was studied the radio active transformations were the only true examples of this type of change. The work of Daniels and Johnston (J. Amer. Chem. Soc. 1921, **43**, 53) on nitrogen pentoxide was fundamental; it showed that the reaction was a true homogeneous gas reaction and marked the start of a series of researches which have built up the modern science of reaction kinetics. The decomposition of nitrogen pentoxide takes place with a change in the number of molecules : $2N_2O_5=2N_2O_4+O_2$. Consequently it could be followed by the pressure differences recorded by a thin all-glass manometer of the Bourdon gauge type which also served as the reaction vessel. The apparatus was evacuated and filled with nitrogen pentoxide vapour to the required pressure through a capillary tube, which was then sealed off. The progress of the reaction at a given temperature was followed and the value of the velocity constant evaluated from the usual formula, but representing concentrations in terms of pressure $pk=\frac{1}{t}\log_e\frac{p_a-p_0}{p_a-p_t}$, where p_0, p_t, and p_a are the pressures at the start, after a time t, and at the end of the reaction respectively; k was found to be independent of changes in the walls of the vessel and its size, and seemed to depend solely on temperature. These results have been confirmed and extended by a number of workers (*see* Hirst, J.C.S. 1925, **127**, 657; Hunt and Daniels, J. Amer. Chem. Soc. 1925, **47**, 1602), who showed that the introduction of foreign gases like carbon monoxide, chlorine, nitrogen and argon produced no change in the value of k. The velocity constant was unchanged by intensive drying, or when the decomposition took place in solution, or by changes of pressure until values of a hundredth of a millimetre were reached, although at still lower pressures k begins to decrease ; *see* Sprenger (Z. physikal. Chem. 1928, **136**, 49); Eyring and Daniels (J. Amer. Chem. Soc. 1930, **52**, 1472) ; and Hodges and Linhorst (Proc. Nat. Acad. Sci. 1931, **17**, 28); Linhorst and Hodges (J. Amer. Chem. Soc. 1934, **56**, 836). Only a small percentage of the molecules are in process of decomposition at any one time and some explanation is needed why the majority remain unchanged. Arrhenius in 1889 suggested that only those molecules with an energy content greater than a limiting value E would react. This conception of the *heat of activation* also enabled him to explain the great influence of temperature on the speed of a chemical process. This effect is generally measured by the *temperature coefficient* which is the change in the velocity of the reaction for an increase of temperature of 10°C. For practically all homogeneous reactions its value is between 2 and 4 ; the vital processes of animal and vegetable metabolism having the same temperature coefficient as the simplest chemical reactions. Arrhenius deduced the following relationship :

$$\frac{d\log_e k}{dt}=\frac{E}{RT^2}$$

or integrating:

$$\log_e \frac{k_1}{k_2} = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k is the reaction velocity constant, R the gas constant, T the absolute temperature, E the heat of activation. By following the reaction at different temperatures the heat of activation for nitrogen pentoxide can be calculated It was found to be 27,400 cals per mol. both for the decomposition in the gaseous state and in solution; indicating that the mechanism is similar in both cases

Three important theories have been advanced to explain the mechanism by which the heat of activation is taken up by the molecule before reacting The first of these is the radiation theory which was put forward by Perrin in 1919, the second the chain theory of Christiansen and Kramers, and the third the collision theory of Lindemann If the molecules were activated by direct collision the reaction would follow a bimolecular course, consequently Perrin (Ann. Physique, 1919, [ix], 11, 1) argued that radiation was the means by which the energy was transferred. Although attractive, the hypothesis was completely discredited when it was shown that nitrogen pentoxide decomposed at the same rate when strongly illuminated with radiation that would supply the above energy ; also that much greater energies could be supplied from light of shorter wave-length without producing any effect Similar results have been obtained for the decomposition of nitrous oxide and of ozone.

Christiansen and Kramers (Z. physikal Chem 1923, 104, 451) suggested that the heat of reaction as well as the original heat of activation are transferred from the product of decomposition to another molecule of the reacting substance thereby activating it. If this were so reaction chains would be set up which would continue until the energy was lost either by collision with an inactive molecule or against the walls of the vessel The chain theory has had much success in explaining photo chemical reactions and certain reactions of other types, but it does not afford a satisfactory explanation of the decomposition of nitrogen pentoxide. If energy is transferred to inert molecules the introduction of a foreign gas should decrease the rate of reaction and make it approach a second order reaction. This has not been observed, and Tolman (J. Amer. Chem. Soc. 1925, 47, 1524) has shown that the homogeneous reaction is endothermic, and that the products are therefore unable to pass on sufficient energy to activate a single molecule of nitrogen pentoxide.

Lindemann (Trans. Faraday Soc. 1922, 17, 598) put forward the basic assumption of the collision theory, which states that the reacting molecules acquire their energy of activation by collision, but that they do not decompose immediately. They will consequently tend to lose this energy, and, therefore, only a percentage of them present at any given moment will succeed in decomposing. Statistically it has been found that no impossible assumptions have to be made to explain reactions by this mechanism, and many experimental results can be explained admirably. If the pressure of a gas is reduced the number of collisions will also fall off until the time between each collision becomes equal to the time between activation and decomposition. At still lower pressures the rate of reaction will depend on the number of collisions and will decrease with the pressure. This has been observed in the case of nitrogen pentoxide by Sprenger (Z. physikal. Chem 1928, 136, 49), and E. F. Linhorst and J. H. Hodges (l c), also by Hinshelwood for several other homogeneous reactions. Hinshelwood also found that the decrease in the rate did not occur if a sufficient amount of hydrogen were present. A purely chemical reaction is ruled out as there is absolutely no effect at higher pressures, but the hydrogen molecule moves at a high speed, and it has five degrees of freedom, which means that it has a large amount of energy available for transfer It is consequently able to keep and to maintain the Maxwell distribution of energy among the molecules of the reacting gas, and hence the supply of active molecules, which would otherwise fall short of the number required to keep the reaction proceeding normally.

For bimolecular reactions, that is, reactions in which two molecules are concerned, the fundamental velocity equation is $\frac{dx}{dt} = k(a-x)(b-x)$, as indicated in the argument on unimolecular reactions Integration of this equation leads to the formula $k = \frac{1}{(a-b)t}\log_e\frac{b(a-x)}{a(b-x)}$. If, however, the two reacting substances have the same initial concentration, that is, if $a=b$, the integrated formula is $k = \frac{1}{t}\frac{x}{a(a-x)}$.

A typical case of a bimolecular reaction, or reaction of the second order, is the saponification of an ester by an alkali. Under suitable conditions of temperature and concentration, the velocity of saponification is measurable, and the progress of the reaction can be determined by extracting samples of the reaction mixture from time to time and titrating for free alkali. The figures in the following table, referring to the saponification of ethyl acetate by sodium hydroxide at 24·7°, will serve to show how far the experimental data are in harmony with the formula just recorded. The reaction mixture in this case was $N/40$ in relation to both ester and alkali, and the figures under $(a-x)$ in the table are the volumes of a standard acid solution required to neutralise 10 c c. of the reaction mixture :

t (min)	$(a-x)$.	$ka = \frac{1}{t}\frac{x}{(a-x)}$
0	8 04	—
4	5 30	0 129
6	4 58	0 126
8	3 91	0·132
10	3 51	0 129
12	3 12	0 131
15	2 74	0 129
20	2 22	0 131

The figures in the last column are satisfactorily constant, and confirm the application of the law of mass action to a bimolecular reaction

The collision theory, indicated in the treatment of unimolecular reactions, can be applied to those that appear to follow a bimolecular course. It suggests that the only difference between the two types is the interval of time between activation and decomposition. If this is small compared with the time between two successive collisions the reaction follows the bimolecular equation, but if large the unimolecular. The full treatment of bimolecular reactions leads into the discussion of *reaction kinetics*, which is beyond the scope of the present article (*cf.* C. N. Hinshelwood, J.C.S. 1935, 1111 ; C. C. Steffens, J. Chem. Educ. 1935, **12**, 115).

The probability of a simultaneous collision between three molecules is relatively small, and few examples of reactions of this type are known. The best known is the combination of nitric oxide and oxygen: $2NO+O_2=2NO_2$ (M. Bodenstein, Z. physikal. Chem. 1922, **100**, 68). The heat of activation of this reaction is of the order of a few thousand calories and the temperature coefficient is actually less than unity. It is difficult to distinguish between a true trimolecular collision and the formation of a complex which then reacts with a normal binary collision (*see* L. S. Kassel, "Kinetics of Homogeneous Gas Reactions"; H. Gershinowitz and H. Eyring, J. Amer. Chem. Soc. 1935, **57**, 985).

Adopting the system previously used we can represent a trimolecular reaction as $A+B+C=D+$etc., and we have $\frac{dx}{dt}=k_3(a-x)(b-x)(c-x)$; this gives on integration

$$k_3=\frac{1}{a'c't}\log_e\frac{a}{a-x}+\frac{1}{a'b't}\log_e\frac{b}{b-x}+\frac{1}{b'c't}\log_e\frac{c}{c-x}$$

where
$$a'=(a-b)$$
$$b'=(b-c)$$
$$c'=(c-a).$$

If all the reactants have the same initial concentration the forms reduce to $\frac{dx}{dt}=k_3(a-x)^3$ and

$$k_3=\frac{1}{t}\frac{1}{2}\left\{\frac{1}{(a-x)^2}-\frac{1}{a^2}\right\}$$

Many reactions are known which are complex in character. One of the best known of these is the formation of hydrogen bromide from the elements. The experimental results obtained by Bodenstein and Lind (Z. physikal. Chem. 1906, **57**, 168) were represented by

$$\frac{d[HBr]}{dt}=k\frac{[H_2][Br_2]^{\frac{1}{2}}}{1+\frac{[HBr]}{10[Br_2]}}$$

The reason for this formula was not given until 1920, when the following series of reactions was disentangled (K. F. Herzfeld, Z. Electrochem. 1919, **25**, 301 ; M. Polanyi, *ibid.* 1920, **26**, 49):

(1) $Br_2=2Br$
(2) $Br+H_2=HBr+H$
(3) $H+Br_2=HBr+Br$
(4) $H+HBr=H_2+Br$
(5) $Br+Br=Br_2$

For a steady condition the concentrations of H and Br will be unchanging, and it can then be shown that these five processes require an expression for $\frac{d}{dt}(HBr)$ identical with that given above. Many reactions occur by means of such "chains" of atoms or activated molecules, and under suitable conditions the average number of steps may become very large. If there is the possibility of the chain "branching" so that one active centre is at some stage converted into two or more the reaction may become infinitely fast and an explosion occurs (*see* N. Semenoff, "Chemical Kinetics and Chain Reactions," Clarendon Press, Oxford, 1935).

Chemical Equilibrium.

The reactions discussed in the foregoing section have all been changes which proceed from left to right until at least one of the substances has disappeared. There are many reactions, however, which do not belong to this type, inasmuch as they come to a stop while all the reacting substances are still present in the mixture. Suppose, for instance, that the reaction between two substances A and B is of this description, and that C and D are the products of the reaction ; then the change proceeds until a state of equilibrium is attained at which all four substances are present. It is further found that if the products C and D are brought together, they react to form the substances A and B, while the final state of equilibrium reached is the same as in the previous case. This is known as a *balanced* or *reversible* reaction, and in the corresponding equation a double arrow is substituted for the usual sign of equality, thus : $A+B\rightleftharpoons C+D$.

The progress of a reversible reaction towards its equilibrium position may be regarded as the resultant of two opposed velocities, one the velocity (v_1) with which the substances on the left react to form those on the right side of the equation, and the other the velocity (v_2) with which the substances on the right side react to from those on the left. Writing the equation in its most general form,

$$mA+nB+\text{etc.}\rightleftharpoons pC+qD+\text{etc.},$$

where m, n, p, q, etc., are the number of molecules of A, B, C, and D respectively that are involved in the transformation. Then if a, b, c, and d be the concentrations of the reactants, and the law of mass action be applied, we can write $v_1=k_1a^mb^n$ and $v_2=k_2c^pd^q$, and the observed velocity is the difference between v_1 and v_2. When the equilibrium condition is reached the forward and the backward reactions will be equal, *i.e.* $v_1=v_2$, and the corresponding concentrations of the materials may be written a_e, b_e, c_e, and d_e. Then since $v_1=v_2$

$$k_1a_e^mb_e^n=k_2c_e^pd_e^q$$

or
$$\frac{k_1}{k_2}=\frac{c_e^p\,d_e^q}{a_e^m\,b_e^n}=K_c$$

where K_c is known as the *equilibrium constant*,

and its numerical value defines the relationship which must exist between the equilibrium concentrations of the substances involved in a reversible reaction. When the materials are gases their concentrations may be measured by their respective partial pressures P_a, P_b, P_c, and P_d, and the equilibrium constant using these units is written K_p.

$$K_p = \frac{P_c^p P_d^q \text{. etc.}}{P_a^m P_b^n \text{. etc.}}$$

If $(a+b-c-d)$ is not equal to zero the numerical values of K_c and K_p will not be identical, but will be related by the following expression provided that the pressures are so low that the gas equation $PV=RT$ can be applied:

$$K_c = K_p(RT)^{(a+b-c-d)}$$

In discussing the application of the law of mass action to reversible reactions with the help of the equilibrium formula, we shall deal first with cases in which the reaction system is homogeneous. As an example, the equilibrium between carbon dioxide, hydrogen, carbon monoxide and water vapour may be considered; the reaction in question is represented by the equation $CO_2+H_2 \rightleftharpoons CO+H_2O$, and is obviously of the type $A+B \rightleftharpoons C+D$. In Hahn's investigation of this equilibrium (Z. physikal. Chem. 1903, 44, 513), platinum was used as a catalytic agent, and on this ground the objection might be raised that the reaction as studied by that investigator is not really homogeneous. A true catalytic agent, however, as will be shown in greater detail at a later stage, does not affect the position of equilibrium in a reversible reaction, but merely lessens the time required for the attainment of equilibrium. The reaction which takes place between carbon dioxide and hydrogen, or between carbon monoxide and water vapour in contact with platinum, may therefore be regarded as a homogeneous reaction. In Hahn's experiments, mixtures of the gases were passed through a heated quartz or porcelain tube containing spongy platinum. Provided that the rate of passage was slow enough to allow the four gases to come into equilibrium with each other, analysis of the issuing gas gave the equilibrium concentrations C_{CO_2}, C_{H_2}, C_{CO}, and C_{H_2O}. The relationship between these required by the law of mass action is $K = \frac{C_{CO} \cdot C_{H_2O}}{C_{CO_2} \cdot C_{H_2}}$, and the validity of the law in the case of this reaction is shown by the fact that the value of K obtained is, for a given temperature, the same when carbon dioxide and hydrogen, in varying proportions, are allowed to react as when carbon monoxide and water vapour are taken as the initial substances. A few figures obtained by Hahn at 986° will serve to support this statement. Mixtures of carbon dioxide and hydrogen, in the proportions shown in the following table, were passed through the reaction vessel, and from analysis of the issuing gas the values of K were calculated by the above formula.

Initial mixture		Equilibrium mixture				
CO_2	H_2	CO_2	CO	H_2O	H_2	K_c
10.1	89.9	0.70	9.46	9.46	80.38	1.59
30.1	69.9	7.18	23.00	23.00	46.82	1.58
49.1	51.9	21.36	27.88	27.88	22.88	1.59
60.9	39.1	34.20	26.61	26.61	12.58	1.64
70.3	29.7	47.66	22.79	22.79	6.76	1.61

Experiments were made, also at 986°, in which the initial mixture contained carbon monoxide and water vapour; the mean value of K *deduced from these experiments* was 1.55, slightly lower than the average of the figures recorded in the table. The discrepancy, however, is not great, and the numerical data quoted suffice to show that the balance established between the four gases, whatever be their initial concentrations, is adequately defined by the mass reaction formula.

The early work on the production of ammonia from the elements may be used to illustrate the changes in K with pressure and temperature. This reaction forms the foundation of the immense industry for the production of synthetic ammonia (*q.v.*) and nitrates which has grown up in the last 20 years. There is a very large patent literature on the subject which cannot be considered here, but a summary by A. Mittasch and W. Frankenburger of the growth and development of the industry will be found in Z. Electrochem. 1929, 35, 920.

Although, as Deville showed 50–60 years ago, even prolonged exposure of ammonia to electric sparks leaves a trace of the gas undecomposed, and a minute quantity of ammonia is formed when a mixture of nitrogen and hydrogen is passed through a heated tube, it was not until the early years of the present century that the reversibility of the reaction was properly appreciated and an attempt made to apply the principles of chemical equilibrium. The physico-chemical investigation of the equilibrium $N_2+3H_2 \rightleftharpoons 2NH_3$ has been carried out mainly by Haber and his collaborators (*see* Z. Elektrochem. 1914, 20, 597; 1915, 21, 89, 128, 191, 206, 228, 241; *also* A. T. Larson and P. L. Dodge, J. Amer. Chem. Soc. 1923, 45, 2918; A. T. Larson, *ibid.* 1924, 46, 367).

Granted that there is a genuine equilibrium between nitrogen, hydrogen, and ammonia, Le Chatelier's principle indicates clearly that at any given temperature increase of pressure will shift the equilibrium position in *favour* of ammonia. This can be expressed by the equilibrium constant in terms of the partial pressures:

$$K_p' = \frac{P^2_{NH_3}}{P_{N_2} \cdot P^3_{H_2}}$$

It is customary to change this slightly by bringing the concentration of ammonia to a unit power, when

$$K_p = \sqrt{K_p'} = \frac{P_{NH_3}}{P^{\frac{1}{2}}_{N_2} \cdot P^{\frac{3}{2}}_{H_2}}$$

Since at high temperatures the equilibrium concentration of ammonia is relatively small, no great error is made, subject to that condition,

by writing $p_{N_2}+p_{H_2}=P$, where P is the total pressure. If, further, the nitrogen and hydrogen have been taken in the exact proportions required by the equation $N_2+3H_2=2NH_3$, these relationships can be coupled with the expression for the equilibrium constant and it follows that $p_{NH_3}=0{\cdot}325K\times P^2$. Hence, for low concentrations of ammonia, the partial pressure of this gas in the equilibrium mixture is proportional to the square of the total pressure.

If x is taken to represent the volume percentage of ammonia in the equilibrium mixture, $x=100\cdot\frac{p_{NH_3}}{P}=32{\cdot}5KP$. This relationship, according to which the volume percentage of ammonia, for small concentrations, should be proportional to the total pressure, is borne out by the figures for the lowest ammonia concentrations in the following table, which is taken from Larson's paper. The figures given refer to the equilibrium percentages of ammonia which were formed from mixtures of 3 parts of hydrogen and 1 of nitrogen at the temperatures and pressures specified.

PERCENTAGE OF AMMONIA AT EQUILIBRIUM.

(Calculated from experimental data obtained at the F.N.R.L.[1])

Temp. °C.	Pressure (atm. abs.) 10	30	50	100	300	600	1,000
200	50·66	67·56	74·38	81·54	89·94	95·37	98·29
250	28·34	47·22	56·33	67·24	81·38	90·66	96·17
300	14·73	30·25	39·41	52·04	70·96	84·21	92·55
350	7·41	17·78	25·23	37·35	59·12	75·62	87·46
400	3·85	10·15	15·27	25·12	47·00	65·20	79·82
450	2·11	5·86	9·15	16·43	35·82	53·71	69·69
500	1·21	3·49	5·56	10·61	26·44	42·15	57·47
550	0·76	2·18	3·45	6·82	19·13	31·63	41·16
600	0·49	1·39	2·25	4·52	13·77	23·10	31·43
650	0·33	0·96	1·53	3·11	9·92	16·02	20·70
700	0·23	0·68	1·05	2·18	7·28	12·60	22·87

[1] Fixed Nitrogen Research Laboratory.

The above figures enable K_p to be calculated between any desired pressure and temperature limits. The type of variation observed when this is done is shown by the following table :

Equilibrium Constant, K_p.

Temp. °C.	Pressure (atm. abs.). 300	600	1,000
450	0·00884	0·01294	0·02328
475	0·00674	0·00895	0·01493
500	0·00498	0·00651	—

It will be observed that quite large variations of K_p with pressure are here beginning to appear. This is due to the very high pressures employed which are causing the gases to deviate very considerably from the conditions laid down when the equilibrium constant was deduced. At pressures of the order of one atmosphere the deviations of K_p are small. It is clear that the highest percentage conversion of nitrogen and hydrogen into ammonia is secured by working at a high pressure and a low temperature. In large-scale work, however, there is obviously a limit to the practicable pressure; nevertheless, modern research has produced alloys from which apparatus can be manufactured to work at approximately 1,000 atm. A lower limit is likewise set to the temperature which can profitably be employed in practice by considerations of velocity. By themselves, nitrogen and hydrogen combine very slowly at temperatures below 1,000°, and it is only in the presence of catalysts such as osmium, uranium and iron that the reaction is reasonably rapid at temperatures where the yield of ammonia is satisfactory. A big yield and a high velocity of reaction cannot be achieved simultaneously, and a balance has to be struck at the temperatures which give the best economic results. On the technical scale the temperature employed is generally 500°–600°C., and the mixed compressed gases are circulated over the heated catalyst in such a way that the ammonia formed is continuously removed by refrigeration or absorption. It should be pointed out that in the manufacturing operation the rate of passage of the gases over the catalyst may be too rapid to permit the reaching of equilibrium at each stage ; it may be more sound economically to maintain the high rate of flow at the expense of the yield (*see* Maxted, J.S.C.I. 1918, 37, 232).

Many other gas reactions of technical importance, as well as of scientific interest, have been investigated and can be represented in terms of the law of mass action. The oxidation of sulphur dioxide by oxygen on a platinum or ferric oxide catalyst is probably the best known. Bodenstein and Pohl (Z. Electrochem. 1905, 11, 373) showed that the constant

$$K_c=\frac{C^2_{SO_2}\cdot C_{O_2}}{C^2_{SO_3}}$$

was independent of the initial concentrations of the reactants, and of the presence of an inert gas—nitrogen. The values of K_p at a series of temperatures are given in the following table :

Temp. °C.	$K\times10^3$.
528	0·015
579	0·077
627	0·32
680	1·12
727	3·54
789	12·6
832	28·0
897	81·6

It will be observed that K is increasing rapidly with temperature; the cause of this change will be dealt with in a later section.

The cases of equilibrium discussed so far have been those in which gases alone are involved. There are, however, many homogeneous reversible reactions in which liquid or dissolved substances take part. A classical example is the reaction between ethyl alcohol and acetic acid, represented thus :

$$CH_3{\cdot}COOH+C_2H_5{\cdot}OH \rightleftharpoons CH_3{\cdot}COOC_2H_5+H_2O$$

If 1 mol. of acid and 1 mol. of alcohol are heated in a sealed tube at 100° for a sufficient time, examination of the reaction mixture shows that it contains $\frac{1}{3}$ mol. each of acid and alcohol, and $\frac{2}{3}$ mol. each of ester and water. If, then, 1 mol-

of ester and 1 mol. of water are mixed and treated in the same way, the equilibrium mixture finally obtained has the same composition as in the first case. The reaction therefore is truly reversible and the equilibrium constant is given by the equation $K=\frac{C_e \cdot C_w}{C_{ac} \cdot C_{al}}$, where C_e, C_w, C_{ac}, and C_{al} are the equilibrium concentrations of the four substances. If v represents the volume of the equilibrium mixture in litres, then for the case where 1 mol. each of acid and alcohol are taken initially $C_e=C_w=\frac{\frac{2}{3}}{v}$ and $C_{ac}=C_{al}=\frac{\frac{1}{3}}{v}$, whence $K=4$ It should be pointed out that the composition of the equilibrium mixture may safely be determined by titrating the free acetic acid, for the velocity of the reaction between ethyl alcohol and acetic acid is negligibly small at ordinary temperatures

If the law of mass action is strictly applicable to the reaction under consideration, then the value of K obtained in experiments in which alcohol and acid are taken in other than molecular proportions should also be 4. Suppose, for instance, that m mols of alcohol are allowed to act on l mol. of acid, and that after equilibrium has been reached, the fraction x of a molecule of ester has been produced, then $C_e=C_w=\frac{x}{v}$, $C_{ac}=\frac{l-x}{v}$, and $C_{al}=\frac{m-x}{v}$; so that

$$K=\frac{x^2}{(l-x)(m-x)}.$$

Instead of observing whether the insertion of the known values of m and x in this formula gives the value 4 for K, the applicability of the mass action law may be tested by taking $K=4$ and ascertaining whether the value of x calculated by the formula for a given value of m is in agreement with the value of x determined experimentally This procedure has been adopted in the actual investigation of the case, with the following results

m	x found	x calc
0 08	0 078	0 078
0 28	0 226	0 232
0 50	0 414	0 423
0 67	0 519	0 528
1 5	0 819	0 785
2 24	0 876	0 864
8 0	0 966	0 945

The excellent agreement of the figures in the second and third columns furnishes a convincing proof of the applicability of the law of mass action. The influence of "mass" or concentration in affecting equilibrium is very clearly illustrated by the numbers quoted in the table, for it will be observed that when the amount of alcohol is great compared with the amount of acid, the latter is almost quantitatively converted into ester; in other words, the yield of ester from acid is nearly theoretical

The solution of an electrolyte in water affords an opportunity of testing the applicability of the law of mass action to another type of equilibrium. After it had been established that the solute was dissociated by solution into two charged ions $AB \rightarrow A^+ + B'$, Ostwald pointed out that the reaction was reversible, since on concentrating the solution the solid solute could once more be separated from it, and that the reaction should consequently be represented $AB \rightleftharpoons A^+ + B'$. Applying the law of mass action we obtain $K=\frac{(A^+)(B')}{(AB)}$. It is more convenient, however, to change the form somewhat and consider a volume v of solution which has dissolved in it 1 g mol. of the electrolyte If a certain fraction x of this material dissociates into ions their concentrations will be given by $\frac{x}{v}$. The amount of the undissociated electrolyte left will be $(1-x)$ and its concentration $\frac{1-x}{v}$. Substituting these values in the first equation, the common formula of the *Ostwald dilution law* is obtained, $K=\frac{x^2}{(1-x)V}$.

This expression was first tested with relatively poorly conducting solutions (weak electrolytes) such as acetic acid and ammonia. The easiest method of doing this was to measure the electrical conductivity of the solution under standard conditions and use this as a measure of the number of charged particles (ions) present in the solution. If the specific conductivity of the solution be multiplied by the reciprocal of the concentration of the electrolyte in gram molecules per litre (dilution) a term is obtained—the equivalent conductivity—which represents the conductivity imparted to a solution under standard conditions by 1 g equivalent of the electrolyte. This quantity Λ should consequently be proportional to the number of ions present and affords a method of determining x, since x will be the ratio of the measured conductivity at a given concentration compared with the conductivity Λ_a that the solution would have when all the salt was ionised; this is visualised as occurring at an infinitely large dilution. Consequently $x=\frac{\Lambda}{\Lambda_a}$ and $K=\frac{\Lambda^2}{\Lambda_a(\Lambda_a-\Lambda)V}$. The following figures show the type of agreement that is obtained when this formula is applied to acetic acid.

c mols /litre	$K \times 10^6$
0 07369	18 45
0 03685	18 51
0 01842	18 49
0 009211	18 49
0 004606	18 51
0 002303	18 49

It will be seen that the mass action law is obeyed with considerable accuracy over the above concentration range. With stronger solutions the deviation becomes larger and K has dropped to 16 5 by the time the acetic acid is $2N$. An equally satisfactory result is obtained for other acids and alkalis provided that K is less than 10^{-4}. Should the dissociation be large, as with strong acids and alkalis or salts, so that Λ approaches 1, the dilution law breaks down

entirely and conditions other than those visualised in the law of mass action determine the equilibrium. The treatment of the properties of strong electrolytes is, however, not within the scope of the present article.

Other properties of aqueous solutions of weak electrolytes may be measured and correlated with the changes in the degree of dissociation expressed by the dilution law. Thus the values of x obtained from the electrical conductivity may be checked by accurate measurements of the freezing-points of the solutions. It also enables an estimate to be made of the distribution of an alkali between two acids of different strengths in the same aqueous solution. If the solution contains equivalent amounts of both the acids and the alkali the base is insufficient to neutralise both acids, and the result is a competition between the two acids, each securing a fraction of the base. A theoretical discussion of this problem shows that if x is the fraction of the base appropriated by the first acid, HA_1, and $1-x$ accordingly the fraction appropriated by the other, HA_2, then, provided the dilution is not too great, $\frac{x}{1-x}=\frac{K_1}{K_2}$. If, therefore, the values of K_1 and K_2 have been determined in the way already described, it is possible to calculate the distribution of the available base between the two competing acids. That this can be done in good agreement with experiment is shown by the following figures:

HA_1.	HA_2.	x calc.	x found.
Dichloracetic acid	Lactic acid	0·95	0·91
Formic acid	Acetic acid	0·75	0·76
Acetic acid	Butyric acid	0·54	0·53

It is evident, then, that a knowledge of the dissociation constant of an acid enables us to calculate relatively the *affinity* or *activity* of this acid for a base. There are other methods for ascertaining the relative affinity or avidity of an acid, methods available in the case of strong acids which do not obey the dilution law, and to which, therefore, no definite value of K can be assigned. Among these methods are the determination of the heat effects accompanying neutralisation (Thomsen), the measurement of the density changes (Ostwald), and the study of the influence of acids in accelerating the inversion of sucrose or the hydrolysis of menthyl acetate. The order of magnitude of the values obtained by these and other methods for the relative affinity of acids is the same, as will be seen by an inspection of the following table:

Acid.	$K \times 100$.	Relative affinity deduced from sucrose inversion.	Relative affinity deduced from density changes.
HCl . . .	—	100	100
HNO_3 . . .	—	100	100
$CCl_3{\cdot}COOH$.	30 (approx.)	75	80
$CHCl_2{\cdot}COOH$	5·14	27	33
$CH_2Cl{\cdot}COOH$	0·155	4·8	7
$H{\cdot}COOH$ . .	0·021	1·5	3
$CH_3{\cdot}COOH$.	0·0018	0·4	1

By a large increase in the concentration of one of the reactants in an equilibrium the dilution of the material with which it combines may be correspondingly reduced. Thus when a $N/4$-solution of sodium acetate is added to an equal volume of $N/4$-acetic acid its hydrogen ion concentration is reduced to about 1/75 of what it was originally. This application of the principles of the mass action conception enables solutions of accurately known hydrogen ion concentration to be obtained (*see* BUFFER SOLUTIONS).

The cases of equilibrium so far discussed have been those which occur in homogeneous systems, but there are numerous cases also of non-homogeneous or heterogeneous equilibrium. The bearing of the law of mass action on reversible reactions of this character will be most readily appreciated by considering one or two examples. The dissociation of calcium carbonate may be taken in the first place. If this substance is heated to 750° in a closed space, it breaks up to some extent into calcium oxide and carbon dioxide: if, on the other hand, carbon dioxide at atmospheric pressure is passed over calcium oxide, heated to the same temperature, the reverse action takes place and calcium carbonate is formed. That is to say, an equilibrium is established which may be represented thus: $CaCO_3 \rightleftharpoons CaO+CO_2$. In applying the law of mass action to this case, we are confronted with the question: What is the concentration or "active mass" of a solid taking part in a reaction? An answer to this question may be reached by supposing that in the gaseous phase of the reaction system there is equilibrium between calcium carbonate, calcium oxide, and the carbon dioxide; that is, each of the solid substances concerned in the reaction is supposed to have a definite, if infinitely small, sublimation pressure at a given temperature, and therefore to be represented in the gaseous phase. On this basis, the equilibrium at a given temperature would be governed by the formula $K_1=\frac{C_2\times C}{C_1}$ where C_1, C_2, and C are the equilibrium concentrations of calcium carbonate, calcium oxide, and carbon dioxide in the gaseous phase. If partial pressures are employed instead of concentrations, the formula would be $K=\frac{p_2 p}{p_1}$. Now p_2 and p_1, being sublimation pressures, have fixed values at a given temperature, and are independent of the absolute amounts of calcium carbonate and calcium oxide present. Hence p=const., and since p_1 and p_2 are negligibly small the partial pressure of the carbon dioxide is practically equal to p_t, the total pressure exerted by the system; so that we may write p_t=const. The application, therefore, of the law of mass action to the dissociation of calcium carbonate leads to the result that at each temperature the reaction system exerts a definite pressure—the dissociation pressure, as it is termed. This statement is valid only on the understanding that the substances involved in the reaction are kept in contact with each other; if provision is made for keeping the pressure of the carbon dioxide permanently below or above the equilibrium

value, then a reaction proceeds until the calcium carbonate (in the first case) or the calcium oxide (in the second case) has disappeared. By artificial alteration of the pressure at constant temperature, therefore, any reaction of the same type as $CaCO_3 \rightleftharpoons CaO + CO_2$ may be made to proceed either from left to right or *vice versa*. The reaction $2BaO_2 \rightleftharpoons 2BaO + O_2$ is also a case where two solids and a gas are in equilibrium with each other, and it may be treated in the same way as the dissociation of calcium carbonate.

Many other examples of the application of the law of mass action to reactions with one or more solids participating are known. Details of these will be found from the bibliography. The chief point that is shown by all of them is that the active mass of a solid is constant and that the chemical equilibrium is the same however much or little of that solid is present in the reaction zone.

Influence of Temperature.—In general the Le Chatelier-Braun theorem enables the prediction to be made that the state of equilibrium for any change varies with the temperature. This theorem states that if a change occurs in one of the factors determining an equilibrium the equilibrium shifts in such a way as to annul the effect of that change. Consequently, if all other factors remain constant, a rise in temperature causes the equilibrium to shift in that direction in which absorption of heat occurs. This change is expressed quantitatively by a relation which is usually called the Van't Hoff equation. By simple thermodynamics it can be shown that $\frac{d \log_e K_a}{dt} = \frac{-Q_p}{RT^2}$, where T is the absolute temperature and Q_p is the heat *evolved* by the reaction at constant pressure when molar quantities interact in the direction left to right. Provided that the active concentrations of the gases can be expressed by their partial pressures the above relation also holds when K_p is substituted for K_a.

Before the Van't Hoff equation can be used to express changes for finite temperature differences it is necessary for it to be integrated, and for this the change of Q with temperature must be known. For differences of temperature up to 10° Q may often be considered as independent of temperature. Then integrating between T_1 and T_2 we obtain

$$\log_{10} K_1 - \log_{10} K_2 = \frac{Q}{4\cdot5787}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The variation of Q with T is given by $\frac{d\Delta Q}{dt} = \Delta C_p$ where C_p represents the difference of the heat capacities of the substances on the right side of the chemical equation compared with those on the left. These heat capacities can be expressed by an equation of the type $C_p = a + \beta T + \gamma T^2$, consequently one can also write

$$\Delta Q = \Delta Q_0 + a^1 T + \beta^1 T^2 + \gamma^1 T^3$$

and this implies that K_p can be represented by an equation like the following:

$$\log_e K_p = \frac{m}{T} + n \log_e T + oT + pT^2 + \text{ etc.}$$

Over a given temperature range the changes C_p must be investigated experimentally to find how many of the above terms are necessary to represent Q in terms of T. In the case of the formation of sulphur trioxide from the dioxide and oxygen Q is found to be a linear function of temperature and is given by the expression $Q = -47{,}300 + 4T$. Substituting this value for Q in the general equation and integrating the following formula is obtained:

$$\log_{10} K = \frac{-10{,}373}{T} - 2\cdot222 \log_{10} T + 14\cdot585.$$

The following figures show that the calculated values of K then agree very satisfactorily with the experimental determinations:

T°C.	Log K found.	log K calc.
528	−4·809	−4·817
579	−4·126	−4·099
627	−3·500	−3·502
680	−2·914	−2·893
727	−2·451	−2·453
789	−1·900	−1·922
832	−1·553	−1·573
897	−1·089	−1·083

In the formation of ammonia from hydrogen and nitrogen, however, Larson (J. Amer. Chem Soc. 1924, 46, 367) found that two further terms were required to express the change of Q with T, i.e.

$$Q = a + \beta T + \gamma T^2 + \delta T^3$$

and consequently

$$\log K_p = \frac{m}{T} + n \log_{10} T + oT + pT^2 + I.$$

Two of these constants o and I were still changing slightly with pressure; at 600 atms. $m = 2{,}074\cdot8$, $n = -2\cdot4943$, $o = 1\cdot0856 \times 10^{-3}$, $p = 1\cdot8564 \times 10^{-7}$, and $I = 3\cdot059$.

Catalysis.

No discussion of reaction velocity or chemical equilibrium would be complete without a reference to the phenomenon of catalysis. It very frequently happens that a chemical reaction, which of itself is extremely sluggish, proceeds with comparative rapidity in presence of some foreign substance—a *catalyst*, as it was called by Berzelius in 1835. Cases of such an acceleration of a chemical reaction have long been known, and in both laboratory and technical processes catalysts are in common use.

A rational quantitative study of catalysis is possible only on the basis of the law of mass action. In the velocity coefficient, as already explained, we have a definite measure of the rate of a chemical change under given conditions. For a given reaction, therefore, which is catalytically accelerated, the value of the velocity coefficient at a given temperature is a measure of the efficiency of the catalyst, and by comparing the values obtained for the velocity coefficient in different experiments, one can find out how the efficiency of a catalyst varies with the conditions under which it works, and how the efficiency of one catalyst compares with that of another working under the same conditions.

General Characteristics of Catalysis.—Ostwald in 1888 formulated the following points by which a catalytic process could be distinguished:

(1) The catalyst should be recovered at the end of the reaction in a chemically unchanged condition even though physical differences as, for example, a larger grain size, can be observed in the material.

(2) The quantity of catalyst should be small compared with the amounts of reactants in which it can induce combination.

(3) In a balanced reaction the final state of equilibrium is unaffected by a catalyst, which should merely affect the rate at which that equilibrium is established.

(4) A catalyst does not initiate a reaction but only increases or decreases its velocity.

The application of these criteria can be illustrated by some work of Bredig on the combination of oxygen and hydrogen on a colloidal platinum surface at room temperatures ; 2·5 c.c. of the colloidal solution containing only 0·17 mg. of platinum were shaken with electrolytic gas and for five successive 10-minute intervals the following decreases in volume were observed: 17·8, 18·0, 19·0, 17·6, and 17·8 c.c. During the next 14 days 10 litres of electrolytic gas were allowed to combine on the platinum surface. The rate was then measured under conditions identical with those in the first determinations and the following diminutions in volume were observed: 20·2, 18·7, 19·5, 19·7, and 20·1 c.c. Thus after transforming nearly 100,000 times its weight of hydrogen and oxygen into water the catalytic surface is still unimpaired. It may be argued that Ostwald's fourth condition is a somewhat pedantic one as the combination of oxygen and hydrogen at room temperatures appears infinitely slow. Since, however, the reaction proceeds at any required rate by suitably regulating the temperature, it is logical to state that the reaction at room temperatures could be detected if sufficient time could be allowed. In the above example the rate of combination is proportional to the amount of catalyst present. This is also the case for the inversion of sucrose by acids where the velocity can be used as an approximate measure of the concentration of hydrogen ions in the solution. It is realised, however, that the action of the negative ions and undissociated molecules is by no means negligible and considerable work has been done in disentangling their respective influences (*see* Glasstone, ' Recent Advances in Physical Chemistry," 1933, Churchill). For many reactions there is no simple relation between the concentration of the catalyst and the velocity of the reaction.

The decomposition of hydrogen peroxide under the influence of colloidal platinum is an illustration of a reaction where the two quantities are still connected in a simple fashion. The course of the decomposition can be followed by removing a definite volume of the reaction mixture from time to time and titrating with potassium permanganate. The rate of the change is in harmony with the formula for a unimolecular reaction, and for each concentration of platinum a definite value of k, the velocity coefficient, can be obtained. The following table contains the values of k corresponding with various concentrations of platinum :

Platinum concentration.	k
$21{\cdot}0\times10^{-6}$	0·072
$10{\cdot}5\times10^{-6}$	0·024
$5{\cdot}2\times10^{-6}$	0·0084
$2{\cdot}6\times10^{-6}$	0·0027

From these figures it appears that when the concentration of the catalyst is doubled, the velocity of decomposition is trebled.

Catalyses and the Law of Mass Action.—The general characteristics of catalysts have been sketched in the foregoing paragraphs, but the phenomena observed are frequently more complex than has been suggested. It appears that the catalyst often works in such a way as to mask the operation of the law of mass action altogether. This is hardly surprising, as the catalyst acts usually by virtue of a surface effect and the concentrations of chemicals there may have no relation to the amounts present in the surrounding gas or liquid. Nevertheless, if a surface acted merely as a means of concentrating the reactants one would expect that the general characteristics of the reaction kinetics would remain unchanged. This is frequently not so, and it appears that the surface effect is usually a specific one. The union of oxygen and sulphur dioxide was first investigated by Bodenstein (Z. physikal. Chem. 1907, 60, 1), and the results show that the velocity of union is independent of the oxygen concentration (except when it is extremely small), proportional to the concentration of sulphur dioxide, and inversely proportional to the square root of the trioxide concentration. This behaviour is obviously quite different from what would be expected under the law of mass action. The explanation adopted by Bodenstein is that the factor which really determines the velocity of reaction is the rate of passage of the sulphur dioxide through a layer of sulphur trioxide adsorbed at the surface of the platinum. From this point of view, what is measured is a diffusion velocity, not a reaction velocity, for it is supposed that the sulphur dioxide and the oxygen, when they have reached the platinum, react with great rapidity. Bodenstein has further shown that the rate of union of the two gases under the influence of other catalysts is governed by the same factors. Not only so, but it has been found that the rate of change in many other heterogeneous catalytic reactions is, in all probability, determined by the physical process of diffusion. Additional support of this view is furnished by the relatively low value of the temperature coefficient in these cases. As already indicated, the velocity of a homogeneous chemical reaction is doubled or trebled for every rise of 10°C., but the value of $\frac{k_T+10}{k_T}$ for a heterogeneous reaction is frequently not much greater than the value (about 1·3) we should expect if the rate of reaction were determined by a diffusion velocity alone.

If there be a layer of sulphur trioxide or similar gas adsorbed as postulated by Bodenstein it is of importance to know how this film is affected

by the pressure of the gas above it. The earliest equation was advanced to represent the amount of gas or liquid taken up by a surface like charcoal. It is known as the Freundlich adsorption isotherm and states that

$$\log C_S = A + B \log C_L$$

where C_S and C_L are the corresponding concentrations in the solid and liquid or gas phases respectively. It is an empirical equation and without theoretical significance. The other relation is an expression of Langmuir's, which was used in connection with his work on reactions in rarefied gases, some of which will be discussed later

His equation is of the form $C_S = \frac{aC_L}{1+bC_L}$ or for a gas $C_S = \frac{ap}{1+bp}$, where a and b are constants and p is the pressure. When applied to specific examples some systems can be represented quite well while sometimes both equations fail completely. *In these cases the form of the adsorption does not appear to be a continuous function of pressure*, which, of course, both the above equations require

An extreme example of this divergence was the discovery of *activated adsorption* by H S Taylor (J Amer Chem Soc 1931, 53, 578, 1614, 1932, 54, 602, Trans Faraday Soc 1932, 28, 247) When hydrogen is taken up by a mixture of manganous and chromous oxides at −78°C the adsorption is rapid, equilibrium is quickly attained and can be represented by an adsorption equation At room temperatures a new effect becomes appreciable which manifests itself as a slow take up of gas which is only measurable in terms of days. Finally at 305°C this slow process has become fast and the amount of hydrogen taken up is nearly 15 times that adsorbed at −78°C Chemical combination is not the explanation, as most of the gas can be pumped off the surface once more. As the influence of temperature on the two processes is studied the van't Hoff equation can be applied for estimating the heat that accompanies the two types of adsorption This is found to be 1,900 g-cal per g mol from −78° to 0°C. and 23,000 from 305° to 444° C. It was therefore suggested that the first type is a pure physical condensation phenomena, whereas the high temperature product consisted of a film of hydrogen molecules that were oriented in the surface and held there by residual valency from the oxide lattice below.

The continuity or otherwise of the adsorption isotherm is of considerable importance in determining what is happening in the surface A continuous line would indicate a physical process of condensation, whereas a series of steps would show the formation of compounds, comparable with the equilibrium between salt and water vapour where a series of hydrates are formed. A remarkable series of discontinuities has been shown in adsorption curves by Allmand and co-workers on a charcoal surface (Proc. Roy. Soc. 1930, 129, 235, 252 ; J. Chem. Physics, 1931, 35, 1692 ; 36, 2272 ; Trans. Faraday Soc. 1933, 29, 458; J. Amer. Chem. Soc 1932, 53, 4453). These results have been confirmed for water and organic liquids on charcoal, for water and carbon tetrachloride on silica gel, and for hydrogen and nitrogen on certain metal surfaces at low temperatures From the point of view of the phase rule there is no doubt that these discontinuities must coincide with the saturation of different specific portions of the solid surface ; but what these regions are is not so clear It is obvious that the different faces of a crystal will have slightly different activities towards an adsorbent, and correspondingly in the charcoal surface there may be points ("active centres") from which adsorption can occur rather more readily than from their surroundings. Such regions would explain the existence of a number of types of activity on a catalytic surface, the work of Vavon and Husson (Compt. rend 1922, 175, 277) being a *good example illustrating this. They were able* to show that propyl ketone is reduced by hydrogen in the presence of colloidal platinum ; if a trace of carbon disulphide is added the *catalyst is poisoned, but is still active for the* reduction of piperonal ; additional carbon disulphide will inhibit this reaction, but nitrobenzene can still be hydrogenated on the surface *Consequently, it appears that there are at least* three types of active centres on platinum for the hydrogenation of organic materials Comparable results have been obtained for other types of reactions.

The work of I Langmuir (J. Amer. Chem Soc 1916, 38, 2221 , *ibid*. 1918, 40, 1361) was of fundamental importance in the development of our knowledge of the combination of gases on metal surfaces He chose to work at low pressures and his apparatus was simple ; a metallic filament electrically heated and suspended in the middle of a reaction bulb which was connected to a suitable manometer and apparatus for introducing and evacuating the gases When a pressure of oxygen of 10^{-6} atm was introduced into the bulb containing a tungsten filament at 3,300°C. the electron emission from the metal was decreased by more than a thousandfold. Consequently even at this high temperature and low pressure an oxygen film could still be formed on the tungsten. This was supported by the observation that 50% of the molecules that collided with the filament succeeded in forming molecules of WO_3 Since there are 3 atoms of oxygen in the oxide and 2 in the gas molecule the third atom must have been on the surface before the collision resulting in reaction occurred. One can deduce, therefore, that at least 50% of the surface is covered by the oxygen film. It is noteworthy that tungsten oxide distils rapidly from a wire at 1,200°C, an indication of the tenacity with which the adsorptive forces are holding the oxygen under the above conditions at 3,300°C A mixture of oxygen and hydrogen was then introduced and the tungsten wire kept at 1,500°C The partial pressure of the oxygen fell, and WO_3 was deposited in the walls of the bulb, but the hydrogen remained unattacked until the oxygen pressure had been reduced to 10^{-4} mm. Then apparently the oxide film breaks, hydrogen can be adsorbed on the filament, and all the oxygen is immediately burnt off. Thereafter the

hydrogen is slowly removed owing to the formation of atoms which then react with the WO_3 on the bulb. It is interesting to note that the character of the oxygen is so changed by adsorption that it is unable to react with hydrogen at 1,500°C. Finally the effect of preferential adsorption on the catalytic surface was shown. Carbon monoxide and oxygen react on a platinum wire at 600°C., but in the presence of cyanogen, which is preferentially adsorbed, the reaction is inhibited until the wire is heated to 1,000°C. This is the temperature at which cyanogen is itself oxidised under the conditions of the experiment, and the combustion of the carbon monoxide then proceeds normally. The above experiments allow of no doubt of the chemical nature of the forces holding the adsorbed material, which should therefore not be more than 1 mol. in thickness. In certain cases this hypothesis has been confirmed by direct experiment and it is now generally accepted.

Langmuir has worked out a series of relationships for the rate of chemical change on a catalytic surface on the basis that one of the reactants or products may be preferentially adsorbed on the surface ; or that two or more of them may compete for the available catalyst. Applying his formula in this way he has succeeded in representing satisfactorily the majority of heterogeneous gas reactions, but for details of the process the books in the bibliography should be consulted.

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CHEMICAL ANALYSIS. This mode of separating a complex material into simpler constituents is *ultimate* when the dissected parts are elementary forms of matter, whereas it is *proximate* when the subdivision consists only in the separation of the original substance into less complicated compounds. The aim of ultimate and proximate chemical analysis is twofold: first, to ascertain the nature of the components of the mixture or complex substance; secondly, to determine the proportions in which these constituents are present. All analytical operations may therefore be classified under two main categories of qualitative and quantitative analysis according as these processes lead simply to the identification of proximate or ultimate constituents of the complex material or to the estimation of the relative proportions of such constituents.

Although written from the viewpoint of technical utility, this article is arranged so as to include references to analytical processes suitable for all the known elementary forms of matter, experience having shown that certain elements formerly regarded as laboratory curiosities have now yielded products of industrial importance.

Systematic study of individual elements and of their typical compounds has revealed the existence of many characteristic reactions exhibited by certain elements and their derivatives in widely varying conditions of combination or association. This circumstance leads to simplifications which are utilisable in both qualitative and quantitative analysis. In qualitative work such special reactions as are not generally interfered with by other elements enable the analyst by a short cut to detect the presence of certain elementary or compound substances without the laborious task of separating these constituents from the other ingredients of the mixture. In this connection, reference should be made to the increasing use of the spectroscope employed not only in detecting various elements but also in estimating their relative proportions (*cf.* " Problems and Methods in Industrial Spectroscopy," by Judd Lewis, J.S.C.I. 1935, 54, 427T). Mention is also desirable of the modern application of organic reagents, many of which form characteristic metallic derivatives often belonging to the class of co-ordination compounds. Such reagents will be referred to at appropriate stages of this article.

In quantitative analysis two essentially different procedures may be adopted. The more fundamental one is *gravimetric* analysis, whereby an elementary or compound constituent of the mixture is isolated and weighed in the form of a definite chemical compound. Having gained this knowledge of distinctive reactions it then becomes possible to employ the second and consequential procedure known as *volumetric* analysis, in which the relative amount of a certain constituent is estimated even in the presence of other components of the mixture under examination by carrying out the chemical changes with definite volumes of solution containing known amounts of reagents. The above-mentioned use of organic reagents has amplified the methods at the disposal of the analyst in both gravimetric and volumetric analysis.

As volumetric processes are generally the more rapid they have been largely developed in industrial laboratories where such quick methods have replaced the more laborious but more exact processes of gravimetric analysis. The loss in accuracy arising from the use of volumetric methods is very small provided that the apparatus employed is accurately calibrated and that experimental conditions are closely defined.

GENERAL OPERATIONS.

SAMPLING.—The sample under examination should be truly representative of the main bulk of the material, otherwise discrepancies arise between the results of different analysts. These differences, often attributed to faulty methods or inaccurate work, are frequently due to imperfect sampling. When liquid, the substance should be thoroughly mixed before any sample is withdrawn. If contained in several vessels proportional quantities should be removed from each, the different portions well mixed, and the final sample taken from this mixture.

In the more difficult case of solids, care must be exercised to secure proper proportions of

large and small, hard and soft fragments. From a ship's cargo portions should be taken from different parts and from railway trucks samples should be collected from the ends and middles of each truck. Hollow augers should be employed for materials contained in bags or barrels, so that long cores may be drawn from different levels. With materials such as alkalis or soap which lose or gain moisture on exposure to air suitable proportions must be extracted from internal sectional portions of the bulk.

In all cases the original samples, broken into small fragments, are thoroughly mixed and one fourth removed for the operation of "quartering." This fraction, when ground to powder, is thoroughly mixed and one fourth again taken for further quartering and the final specimen kept in well closed bottles. Quartering is also effected by spreading out the powder into the form of a flattened cylinder—this being divided radially into four parts The opposite sectors are separated and mixed after which this subdivision is repeated.

With soft and friable materials, pulverisation is effected satisfactorily in porcelain, glass, or even earthenware mortars. When the substance is hard and a fine powder is required the final grinding should be performed in an agate mortar until the powder may be sifted completely through fine muslin Extremely hard inorganic substances should be crushed in a steel mortar (Fig 1) consisting of a strong metallic base with a steel ring or guard within which fits closely a solid steel piston acting as pestle The specimen is placed on the base within the guard ring, the piston is adjusted and driven down on the material by means of a hammer. The final crushing is effected in an agate mortar.

Fig. 1.

Desiccation.—Many substances are hygroscopic, absorbing more or less moisture on exposure to the air, and in order that they may be in a definite condition for analysis it is desirable to dry them either at the ordinary or at higher temperatures depending on the nature of the materials. When a higher temperature would be injurious, the substances are dried in a bell jar or desiccator over concentrated sulphuric acid. The drying takes place more rapidly if the containing vessel is rendered vacuous. Phosphoric oxide is sometimes substituted for sulphuric acid, and where an alkaline drying agent is preferable quicklime is employed.

Substances which are not decomposed at 100° may be dried in an oven provided with a jacket containing water heated to boiling The water level is kept constant by the overflow and inlet arrangement shown at the side in Fig. 2.

When sufficiently stable, the substance may be dried at 110°, since an increase of temperature above 100° greatly reduces the time required. For this purpose the water in the jacket is replaced by toluene, which boils at 110°–111°. Loss by evaporation is prevented by fixing a reflux condenser to the top of the jacket. For still higher temperatures the toluene may be replaced by xylene (b p. 129°) or even by less volatile naphthas. Alternatively, an air oven may be employed to which one of various thermo regulators may be adapted.

Weighing.—The balance and the precautions necessary to ensure correct weighing form the subject of a special article (v. Balance).

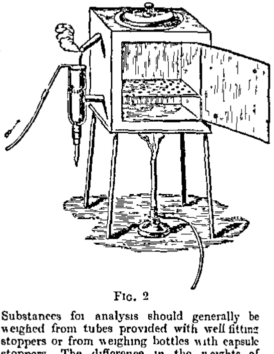

Fig. 2

Substances for analysis should generally be weighed from tubes provided with well fitting stoppers or from weighing bottles with capsule stoppers The difference in the weights of tube or weighing bottle before and after removal of substance gives the weight of the latter taken for analysis. The quantity required depends on circumstances. When constituents present in minute quantities are being estimated a relatively large amount of material becomes necessary, but for estimation of one or more main constituents 1–2 g. of the substance is usually sufficient. The smaller the quantity of matter under treatment the shorter the time required for filtration, washing, and drying, but also the greater are the demands on the skill and accuracy of the analyst Hygroscopic substances and precipitates must be kept in a desiccator, which is usually a glass vessel containing sulphuric acid or anhydrous calcium chloride or alumina. Fig. 3 shows a conveniently portable form of desiccator having a flattened air tight glass cover which is retained in position by a smear of beeswax or grease.

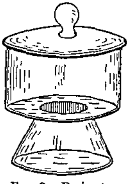

Fig. 3.—Desiccator.

In weighing hygroscopic substances rapidity is highly desirable, and this is achieved by the use of an aperiodic damped balance.

SOLUTION.—In systematic analysis the first operation is to bring the material into solution so that it may be subjected to the action of various reagents. This operation is conveniently effected in flasks or in deep beakers which are inclined at an angle during the process in order to avoid loss by spurting. The opening of the flask or beaker should be suitably covered. If it becomes necessary to dissolve the substance in an evaporating basin this vessel should be covered by a large clock glass. The solvent should be used in concentrated form and as sparingly as possible. The operation may be accelerated by heat. Evaporation to remove excess of solvent should so far as possible be conducted in the same vessel.

EVAPORATION.—The concentration of a liquid may be effected over an ordinary Bunsen flame or rose burner, providing that the liquid does not boil. If the operation is conducted in a crucible, it should be inclined to prevent loss by ebullition, and evaporation is accelerated by inclining the lid of the crucible (Fig. 4) across its opening so as to produce a circulation of air. Other things being equal, rate of evaporation depends on the area of surface exposed, so that evaporation is effected most quickly in shallow dishes especially in a current of air which continually removes the vapour. During the process the contents of the dish or basin should be protected from dust and other extraneous matter by supporting at a distance of two or three inches above the dish a funnel of diameter rather larger than that of the dish. When evaporation over a direct flame is impracticable the basins, dishes, or crucibles should be placed on a water bath, that is, a vessel containing boiling water so that the vessels are heated by the steam. The top of the drying oven shown in Fig. 2 serves as the lid of the water bath when provided with a series of concentric rings to accommodate evaporating dishes of various sizes. Whatever be the form of water bath it should be fitted with a constant level arrangement as in Fig. 2.

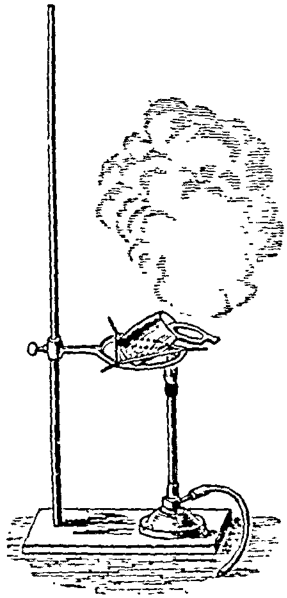

FIG. 4.

PRECIPITATION.—This important operation is conducted in beakers, dishes or conical flasks. Spherical flasks are unsuitable because of the difficulty of removing the precipitate. New glass vessels are appreciably attacked and dissolved by water and still more strongly by alkaline solutions, this action increasing with concentration of solution and time of contact. Acid liquids have less solvent action on glass than alkalis, but nevertheless this attack is notable. For quantitative work special alkali and acid resisting glasses should be used and for this purpose British makers now produce excellent types of glassware.

Porcelain vessels, especially after a short time in use, are not further attacked to any serious extent. Precipitation requiring long heating with alkaline solutions should be conducted in such porcelain vessels or in nickel, silver or platinum dishes.

Silica ware may be used with all acid solutions except those evolving hydrogen fluoride. Except in special circumstances to be indicated subsequently the liquid and reagent are heated separately to boiling and then mixed with continual agitation, since under these conditions precipitation is generally more rapid and complete and the precipitate is produced in a dense and granular form suitable for collection and washing. These operations are begun so soon as the supernatant liquid has cleared. Although a test should always be made with a small further addition of reagent, any unnecessary excess of the latter should be avoided.

In recent practice increasing use is made of centrifuges in promoting the deposition of gelatinous precipitates. When by this means the precipitate has collected at the bottom of the container the supernatant liquid may be decanted without loss of deposited material. The latter may then be mixed with more washing fluid and the centrifugalisation repeated. The separation of precipitate from liquid is usually effected by specially prepared bibulous paper known as filter paper. Swedish filter papers have a well-established reputation. There are also suitable English and German brands. Among the former may be mentioned Whatman paper, which is of excellent quality. These papers have been treated with hydrochloric and hydrofluoric acids and are almost free from inorganic matters. The weight of ash left on ignition of filter paper is always specified by the makers on the cover of the packet. But it is as well to check this value of filter ash by the incineration of a known number of papers.

For quantitative purposes the filter paper is supported in a glass funnel which should be truly conical inside with an apical angle of 60°. Its stem should be long and tapering, not too wide, and with the end cut obliquely to assist in draining away the filtrate.

A circular filter is folded into a quadrant, so that when this quadrant is opened either at one side or more symmetrically by two opposing folds of 45° each, a cone is formed which should fit accurately into the funnel. The size of filter paper should be such that the edge of the cone is about 10 mm. below the rim of the funnel and so that the precipitate does not occupy more than three-quarters of the available space in the filter. The filter cone is moistened with water and adjusted close to the funnel, care being taken to remove any air bubbles entrapped between glass and paper. This precaution facilitates greatly the subsequent filtration. The

edge of the vessel containing precipitate and liquid is slightly greased by rubbing with a finger, the natural grease of which generally suffices for this purpose. The liquid is then decanted into the filter with the aid of a glass rod, leaving the precipitate undisturbed until most of the clear solution has passed through the filter paper. The filter should be kept filled with liquid up to 10 mm. from the top of the paper. Filtration is accelerated by attaching to the stem of the funnel by means of indiarubber tubing a glass tube of 3–4 mm. diameter and not less than 20 cm long bent with a circular loop near its upper end Greater rapidity of filtration is attained by using one of the various types of water pump, the filtrate being collected in a stout walled flask of conical shape with side tube leading to pump The funnel is inserted into a tightly fitting rubber bung. If it is required to collect the filtrate in a basin or beaker this vessel is placed under a tubulated bell jar with ground edge standing on a glass plate, the funnel and side tube being carried on the rubber bung

With considerable reduction of pressure it becomes desirable to strengthen or support the apex of the filter. The necessary tightness is obtained by dropping into the apex of the dry filter already fitted into the funnel two or three drops of the strongest nitric acid. The paper is washed after two minutes and is then ready for use. Alternatively, the apex of the filter paper may be supported by means of a cone of platinum foil dropped into the funnel before the paper is adjusted. This mode of support has now been rendered superfluous by the use of Whatman's hardened filter cones.

The Gooch crucible, constructed in porcelain, silica ware, or platinum, has a perforated bottom lined with thin asbestos mat or exceptionally with filter paper and is now a well recognised means of collecting precipitates. The quality of asbestos is of prime importance and a non-ferruginous amphibole (*v* ASBESTOS) is preferable. Such a variety already prepared by treatment with boiling hydrochloric acid is readily purchasable. This prepared asbestos makes an excellent filter unaffected by the acid and alkaline liquids commonly met with in analysis, it is readily dried and does not alter in weight on ignition. The Gooch crucible is inserted into a cylindrical funnel by means of an indiarubber ring placed between the crucible and the edge of the funnel. The latter is fitted into a filtering flask which is then set in action and water containing the prepared asbestos in suspension is poured into the crucible. A layer of asbestos felt soon covers the perforated bottom of the crucible, and when a mat of sufficient thickness is formed the crucible is drained, dried, ignited, and, after cooling, weighed. During ignition a non-perforated bottom may be fitted on to the crucible in order to protect its contents from the flame gases. The prepared Gooch crucible is now returned to the filter funnel and the precipitate collected in it by the usual procedure. After suitable washing the ignition and weighing are repeated. A Soxhlet tube fitted with a perforated porcelain or platinum disc covered with an asbestos mat is often used as an alternative method of collecting precipitates. Such a tube may be heated in a current of reducing or oxidising gas. Thus cuprous oxide collected in the Soxhlet tube as the result of the interaction of Fehling's solution and a reducing sugar may be reduced by heating in hydrogen to metallic copper or oxidised to cupric oxide by heating in air or oxygen

In the estimation of silver halides, the mat of the Gooch crucible may be of filter paper, and after washing the precipitate successively with water, alcohol, and ether, the crucible need only be dried at 100° before weighing.

Jena-glass or porcelain crucibles fitted with filtering diaphragms of sintered glass or porous porcelain respectively are a more recent improvement. The former have diaphragms of various porosities, but only Nos. 3 and 4 are suitable in analysis; the latter are made in two grades (A2 and A1), having pores of approximately 7 5μ and 6μ respectively. In each case the first-named varieties are for use with coarse precipitates while the others are suitable for finer precipitates, such as barium sulphate or lead chromate

When it becomes necessary to filter while the liquid remains hot, the funnel is placed inside a conical copper jacket filled with water, which is heated by a side tube or more simply a lead pipe is coiled round the funnel and steam is blown through the coil.

In order to remove soluble impurities precipitates are washed with such liquids as water, dilute acids, dilute ammonia, alcohol, or ether This washing is most effectively performed by using small quantities of liquid rather than by applying at once the same volume of liquid. Hot liquids should be used whenever convenient and the precipitate should be washed so far as possible by decantation, only the washing liquor being poured on to the filter. Each quantity of washing liquid should be drained away before the next is added and for this purpose a filter pump is useful. Draining should not, however, be excessive, otherwise channels will form in the precipitate and hinder the uniform penetration by washing liquid of the insoluble mass. Capillary action and evaporation both tend to bring the soluble impurities to the edge of the filter paper and this concentration should be prevented by directing the jet of liquid from the wash bottle to the top of the filter paper. A few drops of the final washings should always be tested for soluble impurities

The filtration and washing of gelatinous precipitates such as aluminium hydroxide or other hydrous metallic oxides are greatly facilitated by adding filter paper pulp to the liquid to be filtered. For this purpose an "ashless" filter paper is cut into small strips and these fragments violently shaken with hot water until they are disintegrated into small fibres.

Drying and Weighing of Precipitate.—Occasionally a precipitate must be dried without rise of temperature, and this is achieved in a desiccator over concentrated sulphuric acid and preferably in a vacuum. When the precipitate is not decomposed at temperatures of 100° to 120° but cannot be ignited it may be collected

on tared filter papers. These are conveniently prepared by folding together two filter papers and by subsequently cutting slips off the apex of the heavier one until they are equal in weight, when they are again folded together, the truncated one outside, and used to collect and wash the precipitate. After drying at the foregoing temperatures the two filter papers are placed on opposite pans of the balance and the weight required to re-establish counterpoise is that of the dried precipitate. Tared filters have now been generally replaced by Gooch crucibles or crucibles with sintered glass or porous porcelain bottoms.

Most precipitates encountered in gravimetric analysis can be brought to constant weight by igniting over a lamp or gas flame. When the precipitate is not easily reducible by carbon it need not be dried. The wet filter enclosing the precipitate after draining on a pad of bibulous paper is placed in a platinum crucible and the latter heated at once with a full flame; the water present assumes the spherical state and the paper smoulders away without spurting. Any slight reduction, such as barium sulphate to sulphide, may be remedied by adding a few drops of sulphuric acid of analytical purity and by then repeating the ignition. With magnesium pyrophosphate, the addition of strong nitric acid serves a similar purpose.

If the precipitate is readily reduced by the carbonaceous matter of the filter paper, precipitate and filter paper must be separated as completely as possible by gentle friction. The precipitate is transferred to the crucible placed on a sheet of glazed paper so that any scattered particles may be transferred quantitatively to the crucible with the aid of a clean feather or camel's hair brush. The filter paper is folded into a cylinder with the apex inside, wrapped in a helix of platinum wire, and set on fire. While burning the platinum cage is held over the crucible, the ignition is completed by touching the residue with the tip of a Bunsen flame, after which the ash is shaken into the crucible. When the precipitate is silver chloride the ash is moistened successively with single drops of concentrated nitric and hydrochloric acids and precipitate and moistened ash are gently ignited in the crucible until the silver chloride begins to fuse at its edges. With silver bromide the treatment is similar except that hydrobromic replaces hydrochloric acid. With silver iodide a few drops of alcoholic solution of iodine replace the mixed acids.

Precipitates which include compounds of arsenic, antimony, bismuth, copper, lead, or tin or of other easily reducible metals, should not be heated in platinum crucibles, since this infusible metal is attacked by the foregoing metals with formation of more fusible alloys. For this reason hot platinum vessels should not be handled with brass crucible tongs although iron ones are permissible. Platinum crucibles are also damaged by exposure to hot caustic alkalis or to smoky flames, especially those formed in the burning of acetylene. Disintegration of the platinum occurs and the surface of the crucible becomes tarnished and dull. The vessel then needs reburnishing before its weight again becomes sufficiently constant for gravimetric operations.

When platinum is inadmissible porcelain crucibles are generally employed. Silica crucibles may be used in the absence of hydrogen fluoride, but these are attacked by the more basic metallic oxides, such as those of copper or nickel. Ferric oxide may be ignited in silica ware providing that filter ash is absent. If present this or similar carbonaceous matter reduces the higher oxide to ferrous oxide, which at the temperature of ignition forms ferrous silicate. Other refractory materials are now available for the production of crucibles and silica may be replaced by the less acidic titania, zirconia, by the amphoteric oxides of niobium and tantalum, and by the basic metallic oxides. Silver and gold crucibles are resistant to the attack of alkalis; tantalum crucibles are recommended as being unaffected by mineral acids excepting hydrofluoric acid.

Heating Appliances.—The ordinary Bunsen burner is still the mainstay for most heating operations, but the Argand modifications introduced by Fletcher are more efficient. A variety of other burners associated with the names of Meker, Fischer, and Teclu are now available for the production of comparatively high temperatures. Electrically heated furnaces are very convenient for heating crucibles at regulated temperatures of 950° to 1,100°; the control is very close and as the heating is highly localised only very little becomes radiated into the laboratory.

Glass vessels are more safely heated on sand baths or in trays containing fusible alloys. They may also be heated by gas or electric current on iron trays or gauze lined with asbestos. In technical laboratories large sand baths or wide iron plates supported on iron legs and heated medially by burners are used to give a graduation of temperatures. Vessels placed at the side of the sand bath or at the edge of the hot plate are subjected to gentle heat but may be raised to higher temperatures as they are moved towards the centre.

Water baths with constant feed arrangements provide the easiest way of heating at 100°; toluene heated ovens give 110°–111°. Higher temperatures are attained with baths of oil, molten paraffin, or a saturated aqueous solution of calcium chloride. Fused mixtures of alkali nitrates give temperatures ranging from 140° to 250° (Maumené, Compt. rend. 1883, **97**, 45), and temperatures approximating to 440° are attained by heating substances in sulphur vapour (Brauner, J.C.S. 1885, **47**, 886).

QUALITATIVE ANALYSIS.

Detection of the constituents of a mixture of chemical substances is based on the fact that almost every metallic or acid radical will give rise to reactions which under certain conditions are characteristic, and accordingly enable one to distinguish this radical from all others. When such tests can be applied directly to the solid material usually at high temperatures they are known as *dry reactions*; whereas when employed in solution they are described as *wet reactions*. The wet and dry

reactions of metallic and acidic radicals are generally, but not invariably, independent of the acidic and metallic radicals with which they are respectively combined

Examination in the Dry Way.

Indications obtained from the dry reactions of a material frequently afford suggestive clues to its composition, but as these tests rarely, if ever, indicate the relative proportions of the various constituents the results must be regarded as preliminary to the more systematic examination of the material in solution. Moreover, *negative indications obtained from dry tests* must not be accepted as final evidence. Nevertheless, a preliminary examination of the original substance should be made in the dry way and if this substance is already in solution, a portion of the liquid should be evaporated to dryness and the residue tested by dry methods. The dry reactions of several admixed substances sometimes mutually interfere with each other, and the evidence is thereby rendered inconclusive, nevertheless, an examination of this kind often gives much information in a short time.

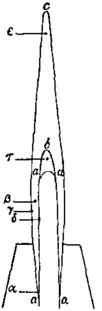

Fig 5.

The most convenient *source of heat for dry tests* is the ordinary Bunsen burner, which consists of a metal tube so arranged that at its base coal gas enters through a jet and air is drawn through holes pierced through the lower part of the tube. The mixture of 1 volume of coal gas with about $2\frac{1}{2}$ volumes of air then produced burns at the top of the tube with a non-luminous flame When the supply of gas is diminished the air supply is reduced by a rotating regulator which partially closes the *inlet holes* The upper part of the burner is generally fitted with a support for a metal cone to protect the flame from draughts

The flame consists essentially of an inner dark zone *a–a* (Fig 5) containing unburnt gas mixed with air and an outer zone or flame mantle *c* in which combustion becomes complete. On partially closing the airholes a *luminous cone* τ appears at the top of the inner zone *a–a*. Closer study of the Bunsen flame shows that several distinct zones exist, each of which can be utilised in producing particular reactions: α is a comparatively *cold zone* at the base of the flame in which metallic salts may be volatilised so as to give flame colorations; δ the *lower reducing flame* at one quarter of the way up and close to the edge of the dark zone a; τ, the *upper* and more powerful *reducing flame* at *the top of the dark cone, obtained by closing* the air hole until the tip of the inner cone just becomes luminous; β the *zone of fusion* at one third of the height of the flame and half way between the inner cone and the flame mantle; γ the *lower* and outer *oxidising flame* at the flame edge just below the zone of fusion; ϵ the *upper oxidising flame* at the extreme tip of the flame

Instead of the Bunsen burner a *blowpipe flame may be used. A mouth blowpipe* consists of a metal tube provided at one end with a mouthpiece, the other end fitting into a small metal box which condenses and retains the moisture of the breath. From this box a second shorter and narrower tube projects at right angles to the first and carries a jet or nozzle (0 4 mm.) of brass *or preferably* platinum This blowpipe and another form due to Black are shown in Fig. 6.

The art of keeping up a continuous air blast through the blowpipe is only acquired by practice. The necessary pressure is produced by distending the cheeks, breathing is carried on through the nostrils, whilst communication between nostril and mouth is cut off by pressure of the tongue against the palate.

A flame suitable for blowpipe work is obtained by dropping *into the tube* of an ordinary Bunsen burner a brass tube, the lower end of which descends to the bottom of the burner and cuts off the air supply, whilst the upper end is flattened and cut off obliquely. The gas flame should be

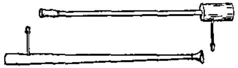

Fig. 6.

smaller than when the burner is used in the ordinary way. As coal gas contains some sulphur discrimination must be exercised in testing for this element. A thick stearin candle may also serve as source of heat or a lamp may be used consisting of a low and rather wide cylindrical metal (brass) vessel open at the top with a relatively broad and flat wick holder attached to its side. *The fuel is* paraffin wax *kept in a molten condition by the heat* of the blowpipe flame, the wick being arranged so that this flame passes over the paraffin wax. A metal cone protects the lamp from dust when not in use. The nozzle being introduced into the lamp flame at a short distance above the *wick, the blast deflects the flame* horizontally so that it becomes long and narrow and this consists of two parts, an outer oxidising flame and an inner reducing flame containing carbon monoxide and hydrocarbons heated to a high temperature.

The following additional appliances are required *for carrying out* dry tests : a small pair of forceps preferably with platinum points; short lengths of platinum wire; charcoal made from fine-grained compact wood; glass tubes of 3 mm. internal diameter and *60–80 mm* long, closed at one end ; similar glass tubes 100–120 mm. long open at both ends and bent slightly in the *middle. The chemical reagents* are borax, $Na_2B_4O_7,10H_2O$; microcosmic salt,

$$Na(NH_4)HPO_4,4H_2O;$$

potassium or sodium cyanide; sodium carbonate or fusion mixture, $NaKCO_3$; potassium nitrate; potassium hydrogen sulphate; cobalt nitrate solution; and litmus papers.

The dry tests are generally performed in the following order:

(1) *Heating in the dry closed tube.*—To avoid soiling the sides the substance is introduced through a roll of stiff paper. The following may be observed:

(*a*) Carbonisation with or without evolution of tarry vapours—*organic compounds.*

(*b*) Condensation of moisture on cooler parts of tube; neutral reaction—*hydrated salts, hydroxides*; acid reaction—*acids, acid salts*; alkaline reaction—*ammonium salts.*

(*c*) Fusion without change of colour—*alkali salts, hydrated salts.*

(*d*) Fusion with change of colour; yellow hot, white cold—*antimony oxide*; yellow hot, dark yellow cold—*bismuth oxide*; yellow hot, red cold—*lead oxide.* Chromates of lead and alkali metal fuse and darken on heating.

(*e*) No fusion, but change of colour; dark yellow hot, pale yellow to white cold—*stannic oxide*; bright yellow hot, white cold—*zinc oxide*; black hot, reddish-brown cold—*ferric oxide*; black hot, bright red cold—*mercuric oxide*; brown, darkening on heating—*cadmium oxide.*

(*f*) Gas evolved: oxygen—*oxides, peroxides, chlorates, bromates, perchlorates, iodates, periodates, persulphates, nitrates*; carbon dioxide—*carbonates, bicarbonates, oxalates*; carbon monoxide (blue flame)—*formates, oxalates*; sulphur dioxide—*acid sulphites, sulphates of heavy metals* (together with sulphur trioxide); cyanogen (peach-coloured flame)—*cyanides of heavy metals*; ammonia—*ammonium salts*; phosphine—*phosphites, hypophosphites*; orange brown vapours—*nitrates, nitrites, bromides*; violet vapour—*iodides*; colourless fuming gas—*hydrated chlorides.*

(*g*) Sublimate: white infusible—*arsenious oxide* (octahedra), *antimonious oxide* (needles), *selenium dioxide, ammonium chloride, ammonium sulphite* (from ammonium sulphate); white fusible—*mercuric chloride, tellurium dioxide, organic acids, molybdenum trioxide* (at high temperatures); coloured, black, or reddish-black—*selenium, mercuric sulphide*; yellow hot, red cold—*mercuric iodide*; reddish-yellow—*arsenious sulphide*; yellow—*sulphur* and *sulphides*; black metallic mirror—*arsenic*; grey metallic globules—*mercury.* These metallic sublimates are obtained more readily on heating the material with alkali cyanide.

Phosphorus compounds are detected by heating in a closed tube with magnesium ribbon and dropping the hot tube into water when inflammable phosphine is evolved with characteristic fishy stench.

(2) *Heating in Open Tubes.*—The open tube being inclined so as to promote a current of air, the changes observed will not be exclusively those of pyrolysis but in many cases will be accompanied by those of oxidation. Sulphides will be oxidised to oxides with evolution of sulphur dioxide; selenium and its compounds will evolve selenious oxide, SeO_2, with pungent odour of horseradish and some deposition of reddish or grey sublimate; arsenic and its derivatives will be oxidised to arsenious oxide, giving a white sublimate.

(3) *Heating on Platinum Wire.*—The wire is cleaned by repeated dipping in hydrochloric acid and heating until no colour is imparted to the flame. Then a minute fragment of the substance is picked up on the end of the wire and introduced into zone *a* of the Bunsen flame. As a coloration is produced only if volatile compounds of the metal are present, the substance should be moistened with hydrochloric acid in order to form the volatile chlorides. A similar result is attained by mixing the substance with moist silver chloride, a compound which while not imparting colour to the flame slowly yields chlorine, thus converting other metals into chlorides. Alternatively, the mixture is supported on a stick of siliceous material such as the support of a vertical gas mantle. Whatever method of support be adopted the substance should be moved from the cooler to the hotter parts of the Bunsen or blowpipe flames so that decreasingly volatile constituents may be revealed successively.

Flame colorations: yellow—*sodium*; orange-red—*calcium*; crimson—*strontium, lithium*; lavender—*potassium, rubidium* and *cæsium*; apple green—*barium*; bright green—*thallium, copper, boric acid*; pale blue—*lead, arsenic, antimony*; deep blue becoming green—*copper halides*; deep blue—*selenium.*

For finer distinctions the direct vision pocket spectroscope is a very useful aid, especially in the case of the potassium sub-family and that of strontium and calcium which exhibit respectively a characteristic blue and a yellowish-green line.

Care should be taken when the compounds of certain heavy metals such as Ag, Cu, Pb, Sn, Sb, and As are present, because these metals have a disintegrating effect on the platinum wire.

(4) *Heating on Charcoal.*—The substance mixed with thrice its weight of dry sodium carbonate, or of a mixture of 2 parts of sodium carbonate and 1 part of potassium or sodium cyanide is placed in a small, shallow hole scooped out in charcoal and heated in a reducing flame. Metallic beads are obtained which are examined for colour, malleability, solubility, and other properties. Films of oxide also arise which coat the charcoal at varying distances from the flame. These films exhibit characteristic appearances. They are best seen when the charcoal is supported on an aluminium plate. A piece of sheet aluminium 12 cm. by 5 cm. is bent at right angles at a distance of 2 cm. from one end, thus forming a ledge on which a small flat piece of charcoal is supported so that the surface of the metal sheet rises vertically behind the ledge. Volatile oxides and sublimates in general condense on to this metallic surface.

The work of the reducing flame is facilitated by adding a fragment of sodium to the substance

supported on charcoal (Parsons, J. Amer. Chem. Soc. 1901, 23, 159).

Reduction effects on charcoal may be obtained by charring a wooden matchstick which has been previously smeared with molten fusion mixture. A portion of the substance under examination is intimately mixed with fusion mixture and heated on the charcoal split in the reducing flame of the Bunsen burner until reduction is complete. The charred matchstick is allowed to cool inside the dark zone, then withdrawn, crushed in a mortar, and the particles levigated with water when the light charcoal floats away leaving heavier metallic particles which may be further examined by heating on asbestos or charcoal in the oxidising flame when sublimates and incrustations are obtained.

Incrustations on charcoal: white crystalline, very volatile=*arsenic*; white, less volatile=*antimony*; orange-yellow hot, pale yellow cold=*bismuth*; pale yellow hot, deep yellow cold, white edge=*lead*; yellow hot, white cold=*zinc*, *molybdenum*; reddish-brown or orange-yellow cold=*cadmium*.

Metallic beads or residues on charcoal: white malleable=*silver*, *tin*, *lead*, red malleable=*copper*; grey brittle=*antimony*, *bismuth*; grey powder, magnetic=*iron*, *cobalt*, *nickel*; non-magnetic=*molybdenum*.

(5) *Cobalt Nitrate Reactions*.—When moistened with this reagent and subsequently heated strongly certain *indefinite* substances acquire characteristic colours: blue infusible mass=*aluminium*; blue fusible=certain *phosphates*, *silicates*, *borates*; green=*zinc*, *titanium*, *tin*; pink=*magnesium*.

(6) *Heating with Borax or Microcosmic Salt*.—A clear bead is formed by fusing in a loop of platinum wire borax, $Na_2B_4O_7,10H_2O$ or microcosmic salt, $Na(NH)_4HPO_4,4H_2O$. A small amount of the substance under examination is picked up on the bead and heated first in the oxidising flame (O.F.) and then after cooling in the reducing flame (R.F.). The colours of the beads should be noted at each stage and also when hot and cold. Excess of substance should be avoided, otherwise the bead becomes opaque and cloudy.

These so called borax and microcosmic beads owe their colours respectively to the formation of certain borates and phosphates of the heavy metals. The excess of boric oxide present in fused borax glass, $Na_2B_4O_7$, unites with a metallic oxide forming the corresponding borate which often has a distinctive colour, such as blue cobalt borate, CoB_4O_4. Microcosmic salt on ignition changes into readily fusible sodium metaphosphate which combines with metallic oxides to form double orthophosphates which often exhibit distinctive colours such as the *green* copper sodium phosphate, $CuNaPO_4$. When a silicate is introduced into the molten metaphosphate the latter withdraws the basic oxide from the former setting free silica which remains undissolved as the so-called "silica skeleton"

$$CaSiO_3 + NaPO_3 = CaNaPO_4 + SiO_2.$$

Borax Beads.—

Outer Flame (O F.)		Inner Flame (R F.)		Metal
Hot	*Cold*	*Hot*	*Cold*	
Yellow	Paler	Green	Bottle green	Iron
Blue	Blue	Blue	Blue	Cobalt
Violet	Reddish-brown	Grey	Grey	Nickel
Amethyst	Amethyst	Colourless	Colourless	Manganese
Yellow	Green	Green	Green	Chromium
Yellow	Colourless	Brown	Brown	Molybdenum
Yellow	Colourless	Yellow to Brown		Tungsten
Yellow	Pale yellow	Green	Bottle green	Uranium
Yellow	Greenish yellow	Brownish	Emerald-green	Vanadium
Yellow	Colourless	Brownish-violet		Titanium
Orange red	Colourless	Colourless	Colourless	Cerium
Green	Bluish green	Colourless	Brown	Copper

Microcosmic Beads.—The colours in the O F. are similar to those in the borax bead, but the reducing effects are less pronounced. In the R.F. *molybdenum* compounds give a green colour; those of *tungsten* a greenish blue tint.

When heated in a microcosmic bead saturated with copper oxide, *chlorides and bromides* evolve a blue and green flame, whereas *iodides* give a green flame.

(7) *Special Dry Tests*.—(*a*) Heating on charcoal with potassium (or cuprous) iodide and sulphur; crimson incrustation=*bismuth*; lemon yellow incrustation=*lead*; greenish-blue fumes=*mercury*.

(*b*) Heating on charcoal with (i) fusion mixture alone (Na_2CO_3,K_2CO_3), and then moistening with dilute acid, hydrogen sulphide evolved=*sulphur compounds*, (ii) with fusion mixture and sulphur a soluble mass giving coloured precipitate with dilute acid, yellow=*tin*; orange=*antimony*. Thus fused insoluble oxides SnO_2 and Sb_2O_4 can then be characterised.

(*c*) Heating with fusion mixture and nitre (KNO_3): soluble green mass=*manganese*, yellow mass=*chromium*.

(*d*) Heating in closed tube with potassium hydrogen sulphate. Gas evolved: carbon dioxide=*carbonates*, *oxalates*; accompanied by charring of the residue=*tartrates*, *citrates*, and many other organic acids; carbon monoxide (blue flame)=*formates*, *oxalates*; sulphur dioxide=*sulphites*, *thiosulphates*; hydrogen sulphide=*sulphides* (not all); hydrogen chloride (fuming in air)=*chlorides* (not all); hydrogen

fluoride (etching glass)=*fluorides*; bromine and hydrogen bromide=*bromides*; iodine=*iodides*; nitrous fumes=*nitrites, nitrates*.

Examination in the Wet Way.

The first essential step in any systematic analytical examination is to bring the material into solution. A metallic substance is treated directly with moderately strong nitric acid, when tin and antimony form oxides which to a large extent remain undissolved; arsenic is oxidised to soluble arsenic acid, other metals are converted into soluble nitrates with the exception of gold and the platinum metals—the so-called noble metals—which are not attacked.

If the substance is not metallic it is first treated with hot water and if anything dissolves (which is ascertained by evaporating a few drops of extract on platinum foil or on a watch glass) the substance is boiled twice or thrice with fresh quantities of water. Any residue is treated with dilute hydrochloric acid and, if still resistant, with the concentrated acid. During this treatment, gases may be evolved which are characteristic thus: carbon dioxide (effervescence) from *carbonates*; sulphur dioxide from *sulphites* or *thiosulphates*; chlorine from *peroxides* or *hypochlorites*; hydrogen cyanide from *cyanides*; hydrogen sulphide from *sulphides* or *hyposulphites*.

Certain chlorides, such as barium and lead chlorides, are very sparingly soluble in strong hydrochloric acid and hence the solution must be diluted before filtering from any residue. Silver, lead, mercurous, and thallous compounds will be converted into insoluble or sparingly soluble chlorides.

Solvent Action of Mineral Acids.—Although it is impossible to give a hard and fast rule as to the mode of applying the following acidic solvents—hydrochloric, nitric, sulphuric and hydrofluoric acids—yet the following considerations will indicate their relative advantages (Noyes and Bray, J. Amer. Chem. Soc. 1907, 29, 137, 481).

Hydrochloric Acid.—(1) *Advantages*: (i) solutions in this acid do not deposit sulphur on treatment with hydrogen sulphide; (ii) its solvent action on lead peroxide, manganese dioxide, and the hydrated oxides of tin and antimony is superior to that of nitric acid; (iii) hydrated silica is readily precipitated on evaporating a solution in hydrochloric acid.

(2) *Disadvantages*: (i) this acid is comparatively useless for alloys; (ii) evaporation of its solution leads to volatilisation of arsenic, germanium, mercury, selenium, and tin as chlorides.

Nitric Acid.—(1) *Advantages*: (i) the best general solvent for metals and their alloys; (ii) oxidises and dissolves insoluble compounds of arsenic, mercury, and selenium without forming volatile derivatives of their elements; (iii) does not cause precipitation of silver, lead, or thallium; (iv) oxidizes sulphides not attacked by hydrochloric and sulphuric acids.

(2) *Disadvantages*: (i) this acid alters the state of combination of many elements, for it oxidises antimonious, arsenious, mercurous, ferrous, and stannous salts; (ii) its solution deposits much sulphur on treatment with hydrogen sulphide; (iii) oxidation of sulphides in presence of barium, strontium, and lead causes precipitation of these metals as sulphates; (iv) nitric acid is less efficacious than hydrochloric acid in rendering silica insoluble. The nitric acid solution of an alloy when evaporated to dryness and heated at 120°–130° may yield partially dehydrated hydroxides of silicon, tin, antimony, titanium, and tungsten in an insoluble condition. When phosphorus or arsenic is associated with tin the insoluble residue may contain stannic phosphate or arsenate (phosphostannic or arsenostannic acid).

Sulphuric Acid.—The dilute acid is of little value as solvent, but hot concentrated acid is useful in certain cases: (i) in bringing certain alloys such as white metals into solution; (ii) in the parting of noble from baser metals; (iii) in rendering soluble certain refractory minerals such as monazite, which contains phosphates of rare earth metals; (iv) destruction of organic matter, when evaporation of a solution of the substance in concentrated sulphuric acid is preferable to ignition, since the latter process renders certain inorganic substances insoluble and leads to loss by volatilisation of such elements as arsenic, mercury, or selenium. Very stable organic substances, such as paraffin wax and cellulose, can be destroyed completely by adding drop by drop a little strong nitric acid to the sulphuric acid solution until the latter acquires a light yellow colour. On dilution with 20 to 30 volumes of water this solution may deposit silica and certain refractory silicates and fluosilicates together with sulphates of calcium, strontium, barium, lead, and insoluble chromic sulphate formed during heating. Moreover, the precipitate may contain basic sulphates of bismuth, antimony, and tin, the dehydrated oxides of the last two metals, and those of aluminium and titanium; (v) insoluble complex cyanides are decomposed by hot concentrated sulphuric acid; alternatively, they may be attacked by aqueous alkali hydroxides to yield soluble alkali cyanides and insoluble metallic hydroxides.

Hydrofluoric Acid.—The residues left from the treatment with the preceding acids are next attacked with a 40% solution of hydrogen fluoride now obtainable in bottles of gutta-percha, phenol-formaldehyde resin, or glass lined with paraffin wax. (1) *Advantages*: (i) many refractory silicates are readily decomposed, the silicon being eliminated completely as gaseous silicon fluoride; (ii) providing that the solutions are not taken to dryness the reducible metals and their compounds may be treated in platinum vessels. (2) *Disadvantages*: (i) glass and silica ware vessels cannot be used with this acid; (ii) its destructive action on animal tissues necessitates an efficient draught cupboard for all operations involving hydrogen fluoride.

Aqua Regia (concentrated hydrochloric acid 3 parts, and nitric acid 1 part) may be employed in attacking substances not dissolved by its two constituents taken separately; it is, however, of little use for colourless insolubles. It readily dissolves gold and platinum, but is less efficacious

in rendering soluble the rarer noble metals such as osmium and iridium.

Treatment of Insolubles.

The substances not readily dissolved by the foregoing acidic reagents are generally regarded as insolubles, although they are divisible into two classes: (i) *pseudo-insolubles*, which are dissolved by special reagents; (ii) *true insolubles*, which are only broken up into soluble compounds through the agency of fused alkali carbonates.

PSEUDO-INSOLUBLES.—*Silver chloride and bromide* soluble in aqueous ammonia. All three silver halides are completely decomposed with zinc and dilute sulphuric acid, metallic silver and soluble zinc halide being produced. *Insoluble fluorides* of the common and rare earth metals are decomposed on heating with concentrated sulphuric acid. *Lead sulphate* soluble in ammonium acetate. *Oxides of antimony* dissolve in hydrochloric and tartaric acids. *Anhydrous chromic sulphate* and *basic bismuth sulphate* when boiled with aqueous sodium carbonate are converted respectively into hydroxide and basic carbonate. These products are then dissolved in dilute mineral acids.

TRUE INSOLUBLES.—These substances are heated with fusion mixture, that is sodium and *potassium carbonates in molecular proportions*—$NaKCO_3$. In the absence of reducible metals, such as silver, copper, lead, or tin, silicates and insoluble sulphates (those of barium and strontium) may be heated with fusion mixture in platinum vessels.

Molybdenum sulphide (indicated previously by dry tests) which would corrode the platinum should be oxidised by adding nitre. Fusions from insoluble silicates are treated directly with hydrochloric acid, when the metals present pass into solution as chlorides, whereas the silica is rendered insoluble by evaporating the acid liquid to dryness. Fusions from insoluble sulphates are extracted with water to remove the soluble alkali sulphates; the residue ($BaCO_3$, $SrCO_3$) is then dissolved in dilute hydrochloric acid. *The insoluble silver halides are decomposed by* fusion mixture yielding the corresponding soluble alkali halides; insoluble lead compounds are decomposed similarly. The ignited oxides of aluminium, antimony, chromium, tin, and titanium rank as insolubles, since they are not readily attacked by fusion mixture but yield to fusion with potassium hydroxide. The oxides of aluminium and titanium may be rendered soluble by heating with potassium hydrogen sulphate.

Special methods for dealing with insoluble oxides of antimony, chromium and tin are indicated among the dry tests (7*b* and *c*). Insoluble compounds (oxides or sulphides) of such easily reducible metals as Ag, Pb, Sn, or Sb are all decomposed and reduced to the metallic state by fusion with sodium or potassium cyanide.

When both aqueous and acidic extracts of the same substance have been obtained the analyst must decide whether these may be mixed or analysed separately. The latter course sometimes gives information as to the distribution of acidic and basic radicals in the original material. If the former alternative is adopted it must be remembered that a hydrochloric acid solution may cause precipitation of lead, silver, thallium, and possibly mercury from an aqueous or dilute acid solution (HNO_3 or H_2SO_4).

Systematic Examination in the Wet Way.—In the systematic separation of acidic and basic radicals the formation of a precipitate at the proper stage is not sufficient proof of the presence of a particular substance, and a characteristic confirmatory test should always be applied. The colour of solutions at different stages in the analytical operations is a valuable indication. *Excess of reagents should be* avoided, but filtrates should always be tested to ensure complete precipitation. Many tests succeed only when a due proportion of reagents is added, and reagents should always be added very gradually. All precipitates which have been subjected to the action of solvents should be thoroughly washed, but in qualitative, as opposed to quantitative, analysis it is not generally desirable that all washings should mix with the filtrate.

Strength of Reagents.—In systematic analysis by the wet way speed and accuracy are increased by working in an approximately quantitative manner. This becomes possible if all the reagents employed are made in solutions which are either multiples or sub multiples of normality. *The dilute acids* (HCl, HNO_3, H_2SO_4, *and* CH_3CO_2H) may conveniently be of $2N$-strength. The alkalis ($NaOH$, Na_2CO_3, NH_3,H_2O, and $(NH_4)_2CO_3$) should then be of the same $2N$ strength. Other reagents may be prepared as follows: Ammonium chloride $4N$-, saturated baryta water, $Ba(OH)_2$, $\frac{1}{5}N$-; saturated lime water $\frac{1}{20}N$-, bromine water $\frac{1}{4}N$-, ammonium sulphate $8N$-, and the other reagents so far as possible made up in normal solutions.

The reaction of the original solution towards litmus paper should be noted and a portion tested for ammonium compounds by heating with aqueous sodium hydroxide or by triturating in a mortar with soda-lime.

In systematic qualitative analysis, advantage *is first taken of similarities existing between* certain metallic radicals which enable these radicals to be segregated into a limited number of groups, the members of each group being subsequently either separated or identified by means of specific *differences* between the properties of the respective compounds of these group members.

In the construction of a scheme of systematic analysis for the more commonly occurring metallic radicals it has long been the practice to divide these radicals into six groups with an alternative division into five groups due to the circumstance that some analysts prefer to add the reagents of Groups III and IV successively without an intervening filtration. The latter procedure was formerly adopted when the conventional reagents were still used in a scheme of analysis applicable in the presence of the less commonly occurring metals. But in more modern practice the older procedure with the following reagents has been discarded in favour of a comprehensive scheme of analysis making use of newer reagents as indicated in a subsequent section of this article (p. 556).

Systematic Separation in the Absence of the Rarer Metallic Radicals.

GROUP I.—Reagent: hydrochloric acid in moderate excess. Precipitate: *silver, lead,* and *mercurous* chlorides.

TABLE I.

WHITE PRECIPITATE BOILED WITH WATER.

<table>
<tr><td colspan="2">Residue: extracted with aqueous ammonia in excess.</td><td rowspan="2">Filtrate: added H_2SO_4, white ppt., $PbSO_4$.

Pb
Confirm for Pb˙ by dry test or with chromate and dithizone tests.</td></tr>
<tr><td>Residue black NH_2Hg_2Cl or $NH_2HgCl+Hg$

Hg˙</td><td>Filtrate acidified with HNO_3 white AgCl.

Ag</td></tr>
</table>

If the original solution was alkaline the precipitate in Group I may contain such sulphides as As_2S_3, Sb_2S_3, or SnS_2, dissolved in aqueous alkali hydroxide or sulphide. This yellow or orange precipitate is examined under Group II. The filtrate from Group I precipitates or the solution itself in absence of such precipitate should be evaporated nearly to dryness to remove nitric acid, since this oxidising agent leads to deposition of sulphur at the next stage.

GROUP II.—Reagent: hydrogen sulphide in acid solution. This is the usual reagent although thioacetic acid and sodium thiosulphate have been recommended as substitutes for the malodorous gas. Precipitate: *sulphides of arsenic, antimony, tin, bismuth, cadmium, copper, lead,* and *mercury.* The solution must be dilute and only moderately acid; it should be saturated repeatedly with the group reagent.

TABLE II.

Group precipitate washed with aqueous hydrogen sulphide and warmed twice with yellow ammonium sulphide, $(NH_4)_2S_x$.

<table>
<tr><td colspan="4">Residue: boiled with dilute nitric acid (1 : 4 by vol.)</td><td colspan="2">Filtrate: acidified with dil. HCl; the ppt. boiled with aqueous $(NH_4)HCO_3$.</td></tr>
<tr><td rowspan="3">Residue: dissolved in aqua regia, excess of acid expelled. $SnCl_2$ added, white ppt. Hg_2Cl_2.

Hg˙˙</td><td colspan="3">Filtrate evaporated to small bulk, diluted with cold water, filtered.</td><td rowspan="3">Residue: dissolve in strong HCl filter from S add to clear solution strips of Pt and Zn, black stain on Pt denotes

Sb

Zn dissolved in HCl and $HgCl_2$ added, white ppt. Hg_2Cl_2 becoming grey (Hg) denotes

Sn</td><td rowspan="3">Filtrate acidified gives yellow ppt. As_2S_3 confirm by dry tests

As</td></tr>
<tr><td rowspan="2">Precipitate $PbSO_4$ soluble in $CH_3{\cdot}CO_2NH_4$. K_2CrO_4 added.

$PbCrO_4$

Pb</td><td colspan="2">Filtrate: add NH_4OH.</td></tr>
<tr><td>Precipitate white $BiO{\cdot}OH$; confirm by dry test.

Bi</td><td>Filtrate blue

Cu; colour discharged by KCN

pass SH_2 yellow ppt. CdS confirm by dry tests.

Cd</td></tr>
</table>

In the separation of As, Sb, and Sn by $(NH_4)HCO_3$ some SnS_2 dissolves and is reprecipitated by acids as a white oxysulphide. Boiling with conc. HCl effects a separation by dissolving the Sn and Sb sulphides, leaving nearly the whole of the As_2S_3 undissolved.

The filtrate from the foregoing sulphides should be examined thoroughly as to the complete precipitation of all metals of analytical Group II. Cadmium is not completely precipitated as sulphide if the solution is too acid, and if quinquivalent arsenic is present the reduction necessary to produce As_2S_3 is not readily occasioned by hydrogen sulphide. If arsenates are suspected they should be reduced by boiling with sulphurous acid or a soluble iodide in acidified solution before the passage of hydrogen sulphide. When these precipitations are complete the solution should be boiled to expel hydrogen sulphide and any iron present is oxidised by addition of nitric acid or bromine water. If organic matter be present it is destroyed either by evaporation to dryness or by treatment with hot sulphuric and nitric acids (*v. supra*). As silica and barium sulphate may be deposited at this stage any colourless precipitate should be collected and examined separately for these insolubles (*q.v.*). A portion

of the oxidised solution should now be tested for phosphate with nitric acid and ammonium molybdate, when a yellow precipitate of ammonium phosphomolybdate indicates the presence of this acid radical and thus determines the subsequent procedure.

GROUP III.—Reagents: Ammonium chloride and ammonium hydroxide. Precipitate: (*a*) In absence of phosphates: *hydroxides of aluminium, chromium,* and *iron.* Some manganese, zinc, and smaller amounts of alkaline earth metals may be co precipitated. (*b*) In presence of *phosphates: phosphates of aluminium, chromium,* and *iron* with those of *Groups* IV, V, and *magnesium.* With excess of ammonium chloride some of the zinc phosphate may remain in solution.

TABLE III (*a*).

(Phosphates absent.)

To the filtrate from Group II after boiling off SH_2 and oxidising with HNO_3 are added NH_4Cl and NH_4OH. Precipitate: *hydroxides of aluminium, chromium* and *iron.* The mixed precipitate is warmed with excess of sodium peroxide and filtered.

Residue: Fe_2O_3,xH_2O possibly containing some MnO_2,xH_2O, dissolved in dil. HCl and confirmed for iron by adding $K_4Fe(CN)_6$. Blue ppt. Fe Fe also confirmed by $KCNS$ red coloration, Fe	Filtrate: divided into 2 parts: (1) boiled with excess of NH_4Cl, white gelatinous ppt. $Al(OH)_3$, confirmed by dissolving in dil. HCl and applying aurin test, (v. *infra*) red lake, Al. Also blue mass with $Co(NO_3)_2$ on charcoal. (2) Acidified with dil. CH_3CO_2H and $Pb(CH_3{\cdot}CO_2)_2$ added, yellow ppt. $PbCrO_4$, Cr

The aluminium is confirmed by dissolving its gelatinous hydroxide in the minimum of hydrochloric acid and adding ammonium aurintricarboxylate (*aluminon*), which furnishes a bright red lake. Confirmatory tests for chromium and iron are described in the special reactions for these metals.

TABLE III (*b*).

(Phosphates present.)

If the original solution was acid, this group precipitate may include any phosphates insoluble in neutral or alkaline solutions.

<table>
<tr><td colspan="2">The sodium peroxide separation applied to one-third of the precipitate.</td><td colspan="2">Remainder of group ppt. dissolved in dilute hydrochloric acid, solution almost neutralised with Na_2CO_3 and treated successively with $CH_3CO_2NH_4$, $CH_3{\cdot}CO_2H$ and $FeCl_3$ until no further precipitation. The deep red mixture is boiled and filtered hot.</td></tr>
<tr><td>Residue: $FePO_4$ dissolved in hydrochloric acid and confirmed as in III (a) for Fe</td><td>Filtrate (i) Add ammonium chloride and boil, $AlPO_4$ confirmed for Al as in III (a) (ii) Yellow solution confirmed as in III (a) for Cr.</td><td>Precipitate: $FePO_4$ and basic ferric acetate neglected.</td><td>Filtrate examined for metals of groups IV and V and for Mg.</td></tr>
</table>

In the foregoing separation the phosphoric acid may alternatively be removed by evaporating the filtrate from Group II to dryness with nitric acid and granulated tin when the insoluble residue consists of metastannic and phosphostannic acids. Phosphoric acid may also be separated as bismuth phosphate, $BiPO_4$ (Keečhan, Z. anal. Chem 1925, 65, 346). To this end, ferric iron is reduced with hydrazine hydrochloride and solid bismuth oxynitrate, $BiO{\cdot}NO_3$, is added to the feebly acid solution The chlorine and phosphate ions are removed so that only 1 mg. of P_2O_5 remains per litre.

GROUP IV.—Reagents: ammonium sulphide or preferably hydrogen sulphide and ammonia. Precipitate: *sulphides of cobalt, manganese, nickel,* and *zinc* (*see* Table IV.)

The black nickelic hydroxide is dissolved in dilute hydrochloric acid and nickel confirmed by dimethylglyoxime (red precipitate). Cobalt may be confirmed by α nitroso-β naphthol (red cobaltic lake) or by sodium nitroso-β naphthol-3 6-disulphonate (nitroso R-salt).

A quicker separation of Group IV sulphides is effected by digesting them with cold dilute hydrochloric acid (1 : 20), when zinc and manganese pass into solution leaving nickel and cobalt sulphides undissolved. *But generally* appreciable traces of the last two metals are found in the filtrate. The rest of the separation is as shown in Table IV:

TABLE IV.

Hydrogen sulphide is passed into the ammoniacal filtrate from Group III. The precipitated sulphides washed and dissolved in hydrochloric acid with addition of $KClO_3$. Solution evaporated to remove excess of acid and excess of $NaOH$ solution added.

<table>
<tr><td colspan="3">Precipitate: Hydrous oxides of Mn, Ni, and Co. Dissolve in HCl, partially neutralise with NH_3,H_2O, add excess of $CH_3\cdot CO_2NH_4$ and pass in SH_2.</td><td rowspan="3">Filtrate $Zn(ONa)_2$. Pass in SH_2 white ppt. ZnS. Ignite on charcoal ZnO yellow to white oxide. Add $Co(NO_3)_2$ ignite again, green mass,

Zn</td></tr>
<tr><td colspan="2">Precipitate: apply borax test: if bead is sherry colour Ni only is present. If bead is blue dissolve ppt. in $HCl+KClO_3$, boil off excess of acid. Nearly neutralise with $NaHCO_3$, boil with excess of KCN, add either $NaClO$ or Br_2,H_2O and $NaOH$ and filter.</td><td rowspan="2">Filtrate: add NH_3 and pass SH_2 pink sulphide, MnS. Fuse with KNO_3, green mass (manganate),

Mn</td></tr>
<tr><td>Black ppt. wash and apply borax test, bead sherry,
Ni</td><td>Evaporate to dryness, apply borax test, blue,
Co</td></tr>
</table>

GROUP V.—Reagents: ammonium carbonate and ammonia. Precipitate: *barium, strontium,* and *calcium* as *carbonates.*

TABLE V.

To the filtrate from Group IV are added ammonia and ammonium carbonate; the solution is warmed, not boiled. The group precipitate is dissolved in dilute acetic acid, and if the flame test gives a green, confirm for barium by adding K_2CrO_4 and filter. If no barium, test at once for strontium and calcium.

<table>
<tr><td rowspan="2">Yellow precipitate: wash, dissolve in HCl. Add dilute H_2SO_4. White ppt. $BaSO_4$,

Ba</td><td colspan="2">Filtrate: add 8N-$(NH_4)_2SO_4$ and a little NH_3,H_2O; boil for 5 minutes; filter.</td></tr>
<tr><td>White precipitate: wash and apply flame test. Crimson flame,

Sr</td><td>Filtrate: add $(NH_4)_2C_2O_4$ white ppt. CaC_2O_4,H_2O. Flame test, brick red,

Ca</td></tr>
</table>

Owing to their close relationship, a sharp separation of these three metals is very difficult. Bray (Tech. Quart. 1908, **21**, 450) recommends an alternative process starting from a group precipitate which contains magnesium as $MgCO_3(NH_4)_2CO_3,4H_2O$, deposited on using ammonium carbonate in presence of alcohol. This precipitate is dissolved in 20 c.c. of 30% acetic acid, solution neutralised with ammonia, reacidified with 3 c.c. of acetic acid, diluted to 40 c.c., 10 c.c. of 20% potassium chromate slowly added and the mixture boiled for 2 minutes; yellow precipitate ($BaCrO_4$). To filtrate 3 c.c. of ammonia are added, diluted to 60 c.c., 50 c.c. of 95% alcohol added; after 10 minutes, yellow precipitate ($SrCrO_4$). To the filtrate 200 c.c. of water are added, the solution boiled and 40 c.c. of 4% ammonium oxalate added; after 10 minutes, white precipitate (CaC_2O_4). From the final filtrate magnesium is precipitated as the crystalline $Mg(NH_4)PO_4,6H_2O$ on adding ammonia and sodium phosphate.

GROUP VI.—A portion of the filtrate from Group V examined for *magnesium* as in the foregoing test; the remainder evaporated to dryness and ignited to expel ammonium salts. The residue dissolved in a small volume of water and tested separately for *potassium* and *sodium*, Table VI.

Ammonium salts must be removed by ignition because they generally interfere with the tests for potassium, but *iconogen*, sodium 1-amino-2-naphthol-sulphonate in 5–10% solution gives with the same strength of potassium salt solutions a colourless crystalline precipitate but does not precipitate an ammonium salt.

Sodium bismuthothiosulphate furnishes a yellow precipitate of $K_3Bi(S_2O_3)_3$; picric acid and sodium hydrogen tartrate also yield characteristic precipitates with potassium salts, but these three reagents give similar precipitates with ammonium salts.

Table VI.

Filtrate from Group V now containing excess of ammonium salts and ammonia is divided into two unequal parts.

The original solution boiled with $NaOH$ or ground up with soda lime, NH_3 evolved Ammonium (NH_4) salts, NH_4.	(1) Smaller portion: add NH_4Cl, NH_4OH and Na_2HPO_4, colourless crystalline precipitate, $Mg(NH_4)PO_4$, $6H_2O$. Mg.	(2) Larger portion: Evaporate to dryness and ignite Apply flame test for Na and K, confirm by dissolving residue in small bulk of water: add (i) H_2PtCl_6—yellow cryst. ppt., K_2PtCl_6. (i (a)) $Na_3Co(NO_2)_6$, yellow ppt., K (ii) Add to another portion, $K_2H_2Sb_2O_7$—colourless cryst. ppt, $Na_2H_2Sb_2O_7,6H_2O$. (ii (a)) Nickel uranyl acetate—yellow ppt, $NaNi[(UO_2)_3(CH_3CO_2)_9]6H_2O$ Na

Group Separations in the Presence of the Rarer Metals.

In the presence of the less commonly occurring elements the group separations tabulated above require considerable modification, but with the addition of a few new procedures they have proved sufficiently elastic and comprehensive to serve as a basis for the identification and characterisation of all the known metals and metalloids. The systematic working out of this complicated analytical problem is largely due to A. A Noyes and his collaborators, and for exact working details reference should be made to their original memoirs (J. Amer. Chem. Soc 1907, **29**, 137; 1908, **30**, 481; 1909, **31**, 611, 625; 1912, **34**, 609; Bray, Tech. Quart. 1908, **21**, 450).

At first these workers retained the old classical separations, with the result that most of the rarer elements were precipitated by the well known reagents (*v supra*) of analytical Groups II, III, and IV, but in the original scheme devised by Noyes, Groups III and IV were merged into one, so that it is chiefly in this comprehensive group that the additional complications are encountered The following is a brief outline of the older methods of separation as adapted to the rarer elements. The numbers of the analytical groups have the same meaning as in the foregoing tables.

Group I.—In addition to mercurous, silver, and lead chlorides, the precipitate may contain thallous chloride and tungstic acid. The former is extracted with hot water, any lead precipitated from the extract as sulphate, the filtrate treated with potassium iodide gives yellow thallous iodide, TlI=*thallium*. Hydrated tungstic acid precipitated by hydrochloric acid from alkali tungstate remains undissolved and is separated from silver and lead by fusion with alkali carbonate. The aqueous filtrate contains alkali tungstate which on boiling with zinc and hydrochloric acid develops a blue coloration=*tungsten*.

Group II.—Hydrogen sulphide in acid solution precipitates selenium, tellurium, molybdenum, gold, and platinum metals. Extraction of the group precipitate with yellow ammonium sulphide brings the greater part of these elements into the tin sub-group, but not wholly, for appreciable quantities of molybdenum, gold, rhodium, palladium, and some ruthenium remain among the insoluble sulphides of the copper sub-group.

A. *Copper Sub group*—The precipitate boiled with dilute nitric acid (1 vol HNO_3, sp gr. 1 20; 5 vols. H_2O) dissolves partially, the solution contains lead, copper, cadmium, and bismuth. The residue, which retains mercury, gold, platinum metals and a trace of tin, is oxidised with bromine water, potassium chloride and hydrochloric acid are added, and the solution concentrated. A yellow crystalline precipitate, K_2PtCl_6=*platinum*. For osmium, palladium, rhodium, and ruthenium, which may be present, see special tests under these metals, p. 578. Excess of acid is expelled from filtrate, which is then rendered alkaline and boiled with excess of oxalic acid; brownish black precipitate=*gold*. Rhenium, which is precipitated in Group II as Rh_2S_7, finds its way into the copper sub group, since this sulphide is only slightly soluble in ammonium sulphide. For special tests, *see under* Rhenium (p. 577)

B. *Tin Sub group*—From the ammonium sulphide solution, dilute acid precipitates sulphides which are digested with boiling concentrated hydrochloric acid; the solution then contains tin and antimony; the residue which retains arsenic and the rarer elements is dissolved by hydrochloric acid and alkali chlorate and the solution concentrated to crystallisation: yellow precipitate, K_2PtCl_6= *platinum*. For iridium and a trace of ruthenium which may be present, *see* special tests under these metals, p. 578. The filtrate treated successively with ammonia and magnesia mixture ($MgCl_2.2NH_4Cl$ with NH_4OH) yields colourless crystals, $Mg(NH_4)AsO_4,6H_2O$

=*arsenic*. After evaporating to remove ammonia the filtrate is boiled with oxalic acid, brownish-black precipitate (*gold*) extracted with hydrochloric acid to dissolve out co-precipitated tellurous acid. The total filtrate is concentrated with strong hydrochloric acid and after removing precipitated potassium chloride treated with slight excess of sodium sulphite, red precipitate =*selenium*. The filtrate is diluted and treated successively with potassium iodide and solid sodium sulphite (excess), the double iodide K_2TeI_6 is reduced, giving black precipitate =*tellurium*. The final filtrate boiled with hydrochloric acid to expel sulphur dioxide is then cooled and treated successively with 10% potassium thiocyanate and stannous chloride (or metallic zinc), red coloration ($Mo(CNS)_4$) soluble in ether=*molybdenum*. Germanium, the nearest analogue of tin, is precipitated as GeS_2 and being soluble in ammonium sulphide passes into the tin sub-group. (For special tests, *see* under the metal, p. 571.)

GROUPS III AND IV.—After boiling to expel hydrogen sulphide, the filtrate from group II is treated with moderately strong ammonia, the colour of the precipitate being noted. The ammoniacal mixture heated nearly to boiling is treated with ammonium sulphide or if nickel is present with hydrogen sulphide. In presence of vanadium, the filtrate from these sulphides is violet-red and on adding hydrochloric acid brown vanadium sulphide is precipitated. The acid filtrate is boiled to expel hydrogen sulphide and treated with ferric chloride and ammonia to precipitate last traces of vanadium. The presence of this metal in the sulphide and ferric hydroxide precipitates is confirmed by dissolving in nitric acid (sp.gr. 1·20), diluting, and adding hydrogen peroxide, an orange-yellow coloration =*vanadium*. The group precipitate is dissolved in hydrochloric acid (sp.gr. 1·12) with addition of nitric acid or bromine water; the solution boiled with hydrochloric acid to remove nitric acid and evaporated to dryness in a platinum dish with 40% hydrofluoric acid. An insoluble residue from the aqueous extract indicates the fluorides of rare earth metals, including scandium, yttrium, thorium, and some fourteen others. These insoluble fluorides are decomposed by hot sulphuric acid and special tests for the rare earth metals are applied to the solution of sulphates (*see* CERIUM; RARE EARTHS, etc.).

The aqueous extract containing the soluble fluorides of all other metals of Groups III and IV is evaporated down successively with hydrochloric and nitric acids; the nitrate solution is treated successively with caustic soda solution, dry sodium peroxide, and aqueous sodium carbonate, a procedure which separates the whole group into two sub-groups with filtrate A and precipitate B. This method is valid even in presence of phosphates.

Sub-group A.—The aluminium sub-group may contain sodium aluminate, beryllate, chromate, peruranate, vanadate, and zincate. This alkaline solution may also contain gallium, its hydroxide being soluble in aqueous caustic soda; indium hydroxide is peptised by this alkali but largely reprecipitated on boiling. Solution A is acidified with nitric acid (sp.gr. 1·42), diluted considerably, treated with sodium hydrogen carbonate in moderate excess and the mixture heated in a stoppered bottle. The precipitate A, containing aluminium, beryllium, and zinc (with gallium and traces of indium) is dissolved in hydrochloric acid and the solution rendered ammoniacal. Zinc remains in solution whereas the hydroxides of the other metals are precipitated. These hydroxides are dissolved in strong hydrochloric acid, ether (1·5 vols.) is added and the cooled solution saturated with hydrogen chloride, colourless crystalline precipitate ($AlCl_3,6H_2O$)=*aluminium*. The ethereal filtrate may now be tested specially for gallium, which may be removed as

$$Ga_4[Fe(CN)_6]_3$$

(*see* special tests p. 568). The ethereal filtrate is evaporated to remove solvent, treated with ammonia, any precipitate is dissolved in 10% sodium hydrogen carbonate, the solution saturated with hydrogen sulphide, the filtrate from sulphide, which may include traces of In_2S_3, is acidified, boiled, and rendered ammoniacal when a white flocculent precipitate $Be(OH)_2$=*beryllium* (confirmed by quinalizarin test, *see* under special tests p. 566).

The filtrate from precipitate A (containing Al, Be, and Zn) is acidified with nitric acid and just neutralised with caustic soda; 2 c.c. of nitric acid (sp.gr. 1·20) and 20 c.c. of 20% lead nitrate are added, yellow precipitate, $PbCrO_4$= *chromium*. The remainder of the lead is now removed by hydrogen sulphide, excess of this gas boiled off, and the solution treated with bromine, excess of which is also removed by evaporation. After neutralising with ammonia, the solution is treated successively with 5 c.c. of 30% acetic acid, 2 g. of ammonium sulphate (or nitrate) and 2 g. of sodium phosphate. On heating the mixture to boiling, a white precipitate, $UO_2(NH_4)PO_4$=*uranium*.

It will be seen from the group separation with ammonium sulphide that vanadium remains in solution as ammonium thiovanadate from which vanadic sulphide is precipitated on acidification. But in the presence of considerable quantities of other metals yielding sulphides in ammoniacal solution some vanadium may be co-precipitated and this portion reappears in the final filtrate from ammonium uranyl phosphate. This solution rendered ammoniacal is successively saturated with hydrogen sulphide, acidified with acetic acid, and boiled, dark brown precipitate, V_2S_5=*vanadium* (*see also* special tests p. 573).

Sub-group B.—This precipitate B may contain hydroxides and phosphates of iron, manganese, cobalt, nickel, zinc (traces), indium, thallium (tervalent), titanium, zirconium, niobium, and tantalum, together with calcium, strontium, barium, and magnesium as carbonates and phosphates. These precipitated hydroxides, carbonates and phosphates are dissolved in hydrochloric acid, the solution evaporated with strong nitric acid and treated with 0·5 g. of solid alkali chlorate, brown precipitate= *manganese*. A portion of the filtrate is tested for phosphoric acid and if present the remainder

is treated with ammonia until nearly alkaline, then boiled with ferric chloride and ammonium acetate. The filtrate contains the common metals of Groups IV and V with magnesium (apply ordinary tests). The precipitate, which consists of the hydroxides, phosphates, and basic acetates of iron, indium, thallium (triadic), titanium, zirconium, niobium, and tantalum, is dissolved in hydrochloric acid (sp gr. 1·12) and the solution shaken with an equal volume of ether. The ethereal extract contains ferric and thallic chlorides; the hydrochloric acid solution retains indium, titanium, zirconium, niobium, and tantalum. Excess of acid is boiled off, the solution almost neutralised with ammonia and treated with hydrogen sulphide, *yellow precipitate*, In_2S_3=*indium (see also special tests p. 568)* The excess of hydrogen sulphide is boiled off and the solution concentrated with sulphuric acid to destroy chlorides; the residue taken up with water and treated with hydrogen peroxide, and subsequently with sodium phosphate, orange yellow coloration=*titanium*, white flocculent precipitate, $Zr(OH)PO_4$= *zirconium*. Filtrate reduced with sulphurous acid when a white flocculent precipitate confirms *titanium*. These separations are complicated by the presence of niobium and tantalum The four precipitated hydroxides of Nb, Ta, Ti, and Zr may be boiled with dilute solution of sodium salicylate and salicylic acid when hydrated titania becomes dissolved The residue is washed with hydrofluoric, nitric, and sulphuric acids and then fused with potassium carbonate. A cold water extraction of the melt dissolves out the two complex potassium salts, $K_8Nb_6O_{19}$ and $K_8Ta_6O_{19}$. On boiling this solution with an acid, hydrated Nb_2O_5 and Ta_2O_5 are precipitated, these are dissolved in hydrofluoric acid and the solution concentrated until K_2TaF_7 crystallises=*tantalum* A portion of the hydrated oxide mixture boiled with zinc and hydrochloric acid, when blue coloration indicates *niobium*. Niobium and tantalum may be separated by a differential hydrolytic dissociation of oxaloniobic and oxalotantalic acids in presence of tannin in a solution slightly acidified with oxalic acid. The tantalum precipitate is light brown, but if contaminated with niobium it is red. Titanium, however, if *present, also gives a red colour (Schoeller et al*, Analyst, 1925, 50, 485; 1928, 53, 264, 565; 1936, 61, 806).

Zirconium minerals contain varying amounts of hafnium, some sources including as much as 30% of HfO_2. This oxide or its derivatives are quite commonly present in commercial zirconium compounds to the extent of 1%. Throughout the preceding analytical process hafnium will accompany zirconium because the two elements are so very similar that they are separated only by special means (*v*. HAFNIUM p 571). The greater volatility of the tetrachloride, $HfCl_4$, the more sparing solubility of the oxychloride,

$$Hf_2O_3Cl_2,5H_2O,$$

and the greater solubility of the hafnofluorides, $(NH_4)_2HfF_6$ and K_2HfF_6, are indicated as offering methods of fractional separation

GROUPS V AND VI.—In the presence of the rarer alkali metals, lithium, rubidium, and cæsium, it is preferable to precipitate magnesium in the calcium group. The filtrate from Groups III and IV concentrated to about 10 c c. is mixed with 30 c c. of 20% ammonium carbonate and 30 c c. of 95% alcohol. Precipitation is complete in 30 minutes, magnesium being present as the double carbonate

$$MgCO_3,(NH_4)_2CO_3,4H_2O.$$

The further treatment of this group precipitate has been already described under Group V (*v*. p. 553), and as an additional confirmatory test for magnesium its blue lakes with quinalizarin or with *magneson* (*p*-nitrobenzeneazoresorcinol) may be employed. The filtrate is evaporated to dryness and ignited; the residue extracted with 10 c.c. of water and to one-third of the extract are added 0 5 c.c. of 10% caustic soda and 2 c.c. of 10% sodium phosphate, the solution is then boiled and mixed with 1 c c. of alcohol, a white precipitate (Li_3PO_4)=*lithium. After removing lithium either as insoluble* fluoride with ammoniacal ammonium fluoride or if present as chloride by means of acetone or other suitable organic solvent, one portion of the solution, containing the remaining alkali metals is tested for sodium by potassium pyroantimonate or by magnesium or zinc uranyl acetate and the other portion for *potassium*, rubidium, and cæsium. These three allied metals give characteristic crystalline perchlorates with perchloric acid, platinichlorides with H_2PtCl_6, and double nitrites with sodium cobaltinitrite. They are further separated through the bismuthonitrites, since $Rb_2NaBi(NO_2)_6$ and $Cs_2NaBi(NO_2)_6$ are only slightly soluble, whereas the corresponding potassium compound is readily soluble. Cæsium can be largely separated from rubidium through the sparingly soluble, white, crystalline, complex salt, $3CsCl,2SbCl_3$, since rubidium is not appreciably precipitated by antimony trichloride under similar conditions. After removing antimony as sulphide the solution is evaporated to dryness and treated with saturated sodium hydrogen tartrate solution. The crystalline precipitate will be $RbHC_4H_4O_6$, which may contain some potassium salt, $KHC_4H_4O_6$. To confirm rubidium, this precipitate is digested in the cold with aqueous 9*N*-sodium nitrite. The extract is treated with saturated $Bi(NO_3)_3,5H_2O$ in 9*N*-acetic acid, yellow crystalline precipitate=*rubidium*. Cæsium is confirmed even in dilute solutions by adding *N*-silicotungstic acid when a fine white precipitate *of* $Ca_8SiW_{12}O_{42}$ *is deposited*.

For precise working details regarding the detection and identification of the rarer elements in accordance with the well established separations into the classical six groups, reference should be made to "Qualitative Chemical Analysis," by R. V. McAlpine and B. A. Soule 1933.

AN ALTERNATIVE SYSTEM OF QUALITATIVE ANALYSIS INCLUDING THE RARER ELEMENTS.

In recent years Noyes and Bray have developed a new system of qualitative analysis which

TABLE 1.

<table>
<tr><td colspan="3">DISTIL with 9N-HBr.</td><td colspan="3">Distillate: Selenium Group. Se, As, Ge.</td></tr>
<tr><td colspan="4">RESIDUE in FLASK. Distil successively with HNO_3 and $HClO_4$.</td><td colspan="2">DISTILLATE: OsO_4.
RuO_4.</td></tr>
<tr><td colspan="6">RESIDUE: Dilute with 12N-$HCOOH$ and boil.</td></tr>
<tr><td rowspan="5">PRECIPITATE.
Tungsten Group.
Sb, Sn, W, and most of Mo. V and Te may also be carried down.

Tantalum Group.
Ta, Nb, and most of Ti, Zr, and Bi may also appear here.

Gold Group.
Hg, Au, Pt, Pd, and possibly Ir and Rh.

Any unattacked material.</td><td colspan="5">FILTRATE: Concentrate and remove any alkali perchlorates. Add HBr to filtrate.</td></tr>
<tr><td rowspan="4">PRECIPITATE.
Thallium Group.
Ag, Tl, and most of Pb.</td><td colspan="4">FILTRATE: Adjust acidity to 0·3N. Pass in H_2S.</td></tr>
<tr><td rowspan="3">PRECIPITATE.
Tellurium Group.
Te, Mo, Re, Ir, Rh.

Copper Group.
Pb, Bi, Cu, and Cd.</td><td colspan="3">FILTRATE: Test portion for Fe and PO_4. To rest add $CH_3{\cdot}CO_2NH_4$ and $Fe(NO_3)_3$. Boil, filter, and add NH_4OH and H_2S to filtrate.</td></tr>
<tr><td rowspan="2">PRECIPITATES as hydroxides, sulphides, or phosphates.

Gallium.
Aluminium Group.
Cr, U, V, Al, Zn, Be. Also W if phosphate present.

Nickel and Zirconium Group.
Mn, Co, Ni, In, Zn, Zr, Hf, Ti.

Rare Earth Group.
Sc, Th, In, and rare earths.</td><td colspan="2">FILTRATE: Evaporate, add NH_4OH and EtOH.</td></tr>
<tr><td>PRECIPITATE.
Alkaline Earth Group.
Ba, Sr, Ca, Mg.</td><td>FILTRATE.
Alkali Group.
Li, Na, K, Rb, Cs.</td></tr>
</table>

includes most of the elements; many new reagents are employed and an elaborate scheme of group separations has been devised. The method requires a considerable amount of technical skill in analysis and consumes a fair amount of time. Only a very brief outline can be given here and for further details reference must be made to the text book compiled by these authors.

Section 1. Preparation of the Solution.—The finely divided sample is first tested for organic matter, ammonia, and for volatile acids. If the first named is present it must be destroyed and this is preferably done by heating on a steam bath with 9*N*-$HClO_4$ and nitric acid. (For the precautions necessary, *see* Section 16 p. 563.) The mixture is finally concentrated to 1–2 c.c. and should contain about 1 g. of the ash.

This material, or the original substance if no organic matter is present, is heated with HBr under a reflux condenser from the top of which leads a delivery tube into a test-tube containing bromine water to trap any H_2S or H_2Se

evolved. If after some minutes' boiling the sample is not all dissolved, a few drops of bromine are added and heating continued on a steam bath. Any residue is now filtered off and the filtrate caught in a 50 c c. distilling flask with ground glass stopper carrying a safety tube; the long side arm of the flask is bent at right angles.

The unattacked material is treated in a dish with HNO_3 to remove bromine and the mixture taken to dryness It is transferred to a platinum dish, digested with a little $27N$-HF on a steam bath for ½ hour, $HClO_4$ and HNO_3 added and the dish heated until fumes of perchloric acid appear It is kept at this temperature until a clear solution is obtained or, otherwise, for ½ hour, the volume of liquor being kept at about 2 c c by addition of $HClO_4$. Finally the mixture is taken to dryness and the residue transferred with the aid of a little water to the distillation flask containing the HBr solution. This solution is now used for the group separations given in Table 1.

Section 2. Selenium Group.—The HBr solution in the distilling flask is heated until only about 3 c c. remain, the distillate being collected in the original test-tube containing bromine water. The contents of this tube are analysed for Se, As, and Ge by reducing free bromine with metabisulphite and then adding $NH_2OH\ HCl$. Red precipitate turning black on heating=Se. Arsenic and germanium are separated by precipitating the former with H_2S in the presence of HF. Removal of the HF and retreatment with H_2S (solution must be about $6N$) now precipitates white GeS_2.

Section 3. Osmium Group.—To the liquor in the distilling flask is added $9N$-HNO_3 (7 c.c), while the side tube is inserted in a test tube containing ice-cold $6N$-$NaOH$. The flask is gently heated until bromine has been evolved, cooled in ice, and Na_2O_2 powder added until the solution is colourless or until a bulk of 1 c.c. has been added. About 4 c c. of liquid is now distilled off, when a yellow to orange solution in test tube denotes Os. Confirm by adding EtOH, filtering if necessary, and saturating slowly with H_2S. Black precipitate=Os.

$9N$-$HClO_4$ is now added to the flask and distillation continued with a fresh test-tube containing sodium hydroxide as before. Red distillate=Ru (a red precipitate may appear due to volatilisation of mercury and must be filtered off). Ru is confirmed by adding EtOH when a black precipitate forms on standing

If the original substance contained organic matter then Os and Ru will have been expelled in destroying this.

Section 4. Separation of Tungsten, Tantalum and Gold Groups.—Even in the absence of Os and Ru it is necessary to heat with HNO_3 and $HClO_4$ in order to convert bromides to perchlorates or hydroxides so that, on dilution, the W and Ta groups are more completely precipitated. Dilution is actually made with 10 c c. of $12N$ $HCOOH$ and the mixture boiled under a reflux condenser for ½ hour, whereby the gold group metals are also precipitated, in addition, this treatment reduces MnO_2, V_2O_5, and chromates which might produce precipitates at this stage. The separation of these various groups from one another and from any unattacked material is given in Table 2.

TABLE 2.

<table>
<tr><td colspan="4">BOIL with $12N$-$HCOOH$.</td></tr>
<tr><td colspan="3">PRECIPITATE: Oxides of W and Ta groups Au group metals. AgBr Sulphates of Pb, Ca, Sr, Ba, Cr, and other unattacked material. Digest with HF on steam-bath, dilute, and filter.</td><td>FILTRATE.
Analyse for all other groups.</td></tr>
<tr><td rowspan="3">FILTRATE.
Tungsten Group
Sb, Sn, W, Mo (V and Te)

Tantalum Group.
Ta, Nb, Tl (Zr, Bi).

See Section 6.</td><td colspan="3">RESIDUE: Au group metals. PbF_2, CaF_2. SrF_2, Ba and Cr sulphates and unattacked material. Boil with Na_2CO_3 Filter and reject filtrate. Treat residue with $HClO_4$.</td></tr>
<tr><td colspan="2">RESIDUE: Au group metals. AgBr $Cr_2(SO_4)_3$ Unattacked material. Heat with aqua regia and HNO_3, filter. Extract residue with hot NH_4OH.</td><td rowspan="2">FILTRATE.
Pb, Ca, Sr, Ba.

Analyse for these.</td></tr>
<tr><td>FILTRATE.
Gold Group.</td><td>Extract.
Add HOAc. White ppt. AgCl.</td></tr>
</table>

Unattacked Material.

Section 5. Treatment of Unattacked Material.—Any substance unattacked by previous reagents is fused with $K_2S_2O_7$ and the aqueous extract of the melt is filtered while residue still remaining is heated with HCl and filtered off. The two filtrates are united,

the acidity adjusted to $0{\cdot}3N$ and H_2S passed in. Any precipitate of Se, As, etc., is treated as original material, being analysed as far as the H_2S groups, while the filtrate is examined for later groups beginning with thallium. Residue from the bisulphate fusion is treated as in Table 2 and unattacked material (Ir, SnO_2, $Cr_2(SO_4)_3$, silicates) is fused with Na_2O_2. The aqueous extract of the fusion is boiled, neutralised with HCl, and then made acid with this reagent after adding 1 c.c. of alcohol. This solution is now treated in the same manner as was the solution from the previous fusion excepting that precipitation with H_2S is made under pressure to ensure complete deposition of the sulphides of platinum metals.

Section 6. Analysis of Tungsten and Tantalum Groups.—(*a*) The filtrate from the digestion with HF (Table 2) is fumed with H_2SO_4, diluted, and the solution made alkaline with NH_4OH. Freshly prepared $(NH_4)_2S$ is added and the mixture heated for ½ hour in a pressure bottle in hot water. A precipitate indicates the presence of Ta, Nb, Ti, Zr, Bi, or much V, and if it is considerable then more sulphide is added and the heating repeated. The final residue is filtered off, washed, and examined by (*b*), (v. *infra*).

The filtrate (thio salts of Sb, Sn, W, Mo, Te, V, and also $(NH_4)_2HPO_4$)) is poured into dilute acid, any precipitate being collected, dried, and ignited in H_2S to produce lower valency sulphides. Sb and Sn are then removed with concentrated HCl and tested for by usual methods. The residue (WS_2, MoS_2, Te, V_2S_3) is dissolved in aqua regia, the solution evaporated and the residue boiled with $2N$-HCl; yellow residue$=H_2WO_4$, which is confirmed. Mo and Te are now removed by means of H_2S under pressure; $VOCl_2$ being unaffected is tested for in the filtrate. The sulphide precipitate is again dissolved in aqua regia, evaporated and treated with HCl, KSCN, and Zn; black ppt.$=$Te: red solution$=Mo(SCN)_4$.

(*b*) The tantalum group precipitate obtained above may contain TiO_2, Ta_2O_5, Nb_2O_5, Ti, and Zr with PO_4 or VO_4, Bi_2S_3, and is analysed as in Table 3.

TABLE 3.

<table>
<tr><td colspan="5">Boil with Na salicylate+salicylic acid for 2 hours (30 c.c. $3N$-Na_2CO_3+15 g. salicylic acid). Filter.</td></tr>
<tr><td colspan="2" rowspan="2">FILTRATE: Ti salicylate, H_3VO_4, H_3PO_4. Concentrate, add H_2SO_4, extract salicylic acid with ether. Add *NaOH*. *Boil.*</td><td colspan="3">RESIDUE: Ta_2O_5, Nb_2O_5, $Zr(HPO_4)_2$, Bi_2S_3. Fuse with K_2CO_3, add cold H_2O. Filter.</td></tr>
<tr><td colspan="2">FILTRATE: $K_8Ta_3O_{19}$, $K_8Nb_3O_{19}$, K_2HPO_4. Saturate with SO_2, heat, and filter.</td><td rowspan="2">RESIDUE: ZrO_2, Bi_2O_3. Fuse with $K_2S_2O_7$, add H_2O and H_2S. Filter off black Bi_2S_3.</td></tr>
<tr><td>PRECIPITATE: TiO_2. Dissolve in HNO_3, add H_2O_2.</td><td>FILTRATE: Na_3VO_4, Na_3PO_4. Add HCl, NH_4OH, and H_2S.</td><td colspan="2">PRECIPITATE: Ta_2O_5, Nb_2O_5. Dissolve in HF, add K_2CO_3, evaporate, ignite, add water and boil. Filter.</td></tr>
<tr><td>ORANGE SOLUTION, $TiO_2{\cdot}H_2O_2$. Add Na_2SO_3 and Na_2HPO_4.</td><td>VIOLET-RED SOLUTION, $(NH_4)_3VS_4$</td><td rowspan="2">PRECIPITATE: $2K_2TaF_7$, Ta_2O_5.</td><td>FILTRATE: K_2NbOF_5. Fume with H_2SO_4, add NH_4OH, boil. Acidify with H_2SO_4 and boil.</td><td>FILTRATE: $ZrOSO_4$. Boil, add H_2O_2 and Na_2HPO_4.</td></tr>
<tr><td>PRECIPITATE: $Ti(HPO_4)_2$.</td><td></td><td>PRECIPITATE: Nb_2O_5. Confirm.</td><td>PRECIPITATE: $Zr(HPO_4)_2$.</td></tr>
</table>

Section 7. Gold Group.—(Hg, Au, Pt, Pd, and possibly Ir and Rh as chlorides.) The filtrate containing this group (*see* Table 2) is shaken with ethyl acetate which extracts $HgCl_2$ and $AuCl_3$. This extract is now shaken with $3N$-NH_4Cl, whereby the mercury is removed and confirmed. The acetate layer is washed with $3N$-HCl, evaporated, and the residue is tested for Au.

The aqueous layer from the ester extraction is evaporated almost to dryness with a little HCl; the residue if colourless is rejected, but if coloured it is treated with a drop or two of $6N$-HCl and a little solid NH_4Cl; yellow ppt.$=$Pt; black ppt.$=$Ir; red ppt.$=$Pt+Ir. This precipitate is taken up in aqua regia, evaporated to dryness, and water added, followed by $NaHCO_3$ until alkaline and a little Br water;

blue colour changing to black ppt. on warming = Ir. Platinum is confirmed in the filtrate.

The filtrate after the removal of Pt and Ir, and which may contain $(NH_4)_2PdCl_4$ and $(NH_4)_3RhCl_6$, is saturated with Cl_2 in a small bottle, the latter being then stoppered and allowed to stand for ½ hour. Red ppt. = Pd. A red or orange filtrate after expelling Cl_2 indicates Rh which, however, must be confirmed.

Section 8. Thallium Group (*see* Table 1).—*The perchloric acid solution after the removal of the* W, Ta, and Au groups is treated with HBr to precipitate Ag, Tl, and most of the Pb as bromide. The last two are extracted successively with hot water and bromine solution and silver confirmed in the residue in the usual way. In the combined extracts Pb is removed as sulphate while Tl is confirmed by reducing $TlBr_3$ with SO_2 and KI; yellow ppt. = TlI.

Section 9. Tellurium and Copper Groups.—The filtrate from the previous group is evaporated to slight fumes of $HClO_4$, diluted, and its acidity adjusted to 0·3*N*— using for this purpose an indicator made from 25% methyl violet in alcohol which changes from blue to green between 0·15 to 0·18*N*- acid. A little ammonium chloride is added and H_2S passed into the warmed solution until it cools. The resulting precipitate of Te, Mo, Ir, Rh, Re, Pb, Cu, and Cd sulphides is removed, dissolved *in* aqua regia and the solution taken to dryness. The residue is dissolved in 6 c.c. of conc. HCl and the solution is saturated with SO_2 and filtered if necessary. The filtrate is diluted with 20 c.c. H_2O, again treated with SO_2, and heated. Any black precipitate of Te is removed and the remaining solution is examined according to Table 4.

TABLE 4.

<table>
<tr><td colspan="5">FILTRATE after removal of Te. Evaporate almost to dryness, add a few drops of HNO_3 and again take to dryness. Add 6N-HCl and extract with ether.</td></tr>
<tr><td rowspan="2">ETHER LAYER. $MoO_3,2HCl$. Evaporate.</td><td colspan="4">WATER LAYER: Evaporate, add H_2O, CH_3COOH, and $NaNO_2$. Heat at 60°–70°, make alkaline with NaOH.</td></tr>
<tr><td colspan="3">FILTRATE: $Na_3Ir(NO_2)_6$, $Na_3Rh(NO_2)_6$, $NaReO_4$. Add HCl, evaporate, add Na_2CO_3 and Br_2.</td><td>PRECIPITATE Pb, Bi, Cu, Cd.</td></tr>
<tr><td>RESIDUE: Blue. $Mo_2O_5 \cdot xMoO_3$. Add HCl, KSCN and Zn.</td><td colspan="2">PRECIPITATE. IrO_2 (blue-black), RhO_2 (green). Take up in HBr, evaporate with aqua regia. Add 2 drops of 6N-HCl and solid NH_4Cl. Heat on steam-bath.</td><td rowspan="3">FILTRATE: $NaReO_4$. Add 12N-HCl, evaporate and boil. Reduce with a little $N_2H_4 \cdot HCl$ and $NaHSO_3$, boil and filter neglecting any ppt. Add 12N-HCl until solution is 6N and pass in H_2S.</td><td rowspan="4">Analyse by usual methods</td></tr>
<tr><td rowspan="3">RED COLOUR: $Mo(SCN)_4$</td><td rowspan="3">PRECIPITATE: Black $(NH_4)_2IrCl_6$</td><td>FILTRATE: $(NH_4)_3RhCl_6$. Add NH_4OH, evaporate, add HCl.</td></tr>
<tr><td rowspan="2">PRECIPITATE: Yellow, $[RhCl(NH_3)_5]Cl_2$.</td></tr>
<tr><td>PRECIPITATE: Black ReS_2.</td></tr>
</table>

Section 10. Removal of Aluminium, Zirconium, Nickel, and Rare Earth Groups.—The filtrate from the H_2S precipitate is tested for iron and phosphate on a small portion, while the bulk of the solution is boiled and then oxidised with a little bromine, any excess of this reagent being removed. The acidity of the solution is reduced (with 4 c.c. of 6*N*-NH_4OH), after which it is submitted to the basic acetate process with ammonium acetate and ferric nitrate. Sufficient iron is added to combine with all the phosphate although rare earth phosphates may still precipitate as such, while Zn, Co, Ni, Be, and U may also be carried down. The precipitate containing Fe, Ga, Cr, V, W, Al, In, Zr, Ti, PO_4 is dissolved in HCl, evaporated, and the residue taken up in 7*N*-HCl. $FeCl_3$ and $GaCl_3$ are extracted with ether and are separated by reducing the iron to $FeCl_2$ when only $GaCl_3$ dissolves in *the ether*. The separation is not clean and the final traces of iron are removed by dissolving the gallium in 0·3*N*-NaOH.

The aqueous layer, after the extraction of Fe

and Ga, is evaporated with HNO_3, sodium hydroxide is added followed by sodium peroxide. On boiling the mixture the aluminium group (Cr, U, V, W, Al, Be, Zn, and PO_4) dissolves while the Zr group (Zr, In, Ti) together with Co, Ni, Zn, and the rare earths remain behind.

The filtrate from the basic acetate separation is made alkaline with ammonia, boiled, and saturated with H_2S. Any precipitate indicates Be, Cr, or rare earths as hydroxides or Mn, Zr, Co, Ni, or U as sulphides. It is dissolved in HNO_3, evaporated, and treated with $NaOH + Na_2O_2$ as above. The Ni and rare earth groups are precipitated, while any aluminium group metals are dissolved and the filtrate containing them is added to that previously obtained.

Section 11. Aluminium Group.—The combined filtrates from the sodium peroxide treatments in the previous section are acidified with nitric acid in the cold, diluted, neutralised with solid $NaHCO_3$ and 1·5 g. excess is then added together with a little H_2O_2. The mixture, in a closed bottle, is heated in a water bath when Al, Zn, and Be are precipitated. A little U may be carried down, while if much U and V are present then uranyl vanadate will be deposited also. The precipitate is dissolved in $6N$-HCl, $1\frac{1}{2}$ volumes of ether added, and the solution saturated with HCl gas. White crystalline precipitate $= AlCl_3 \cdot 6H_2O$, which must be confirmed. The filtrate is evaporated and the residue dissolved in a little water; addition of ammonia now causes the deposition of Be and U as hydroxide and diuranate respectively, while Zn is tested for in the solution. Beryllium is separated from uranium by evaporating the precipitate with acetic acid and extracting basic beryllium acetate with chloroform. Uranium is sought for in the aqueous liquor.

The filtrate from the carbonate-peroxide procedure may contain sodium chromate, vanadate, tungstate, phosphate, and uranyl vanadate, and is examined according to Table 5.

TABLE 5.

<table>
<tr><td colspan="4">Add HNO_3 and $Pb(NO_3)_2$.</td></tr>
<tr><td rowspan="4">PRECIPITATE: Yellow, $PbCrO_4$. Confirm Chromium.</td><td colspan="3">FILTRATE: $UO_2(NO_3)_2$, H_3VO_4, $H_3PO_4(WO_3)_{12}$, $Pb(NO_3)_2$. Remove Pb with H_2S and oxidise solution with Br_2. Neutralise and add $CH_3 \cdot COOH$ and Na_2HPO_4.</td></tr>
<tr><td>PRECIPITATE: $UO_2(NH_4)PO_4$. Dissolve in HCl, evaporate and add $K_4Fe(CN)_6$.</td><td colspan="2">FILTRATE: H_3VO_4, $H_3PO_4(WO_3)_{12}$. Add ammonia, saturate with H_2S. Pink or violet-red solution denotes vanadium. Acidify with nitric acid.</td></tr>
<tr><td rowspan="2">PRECIPITATE OR COLOUR: Dark red, $K_2(UO_2)Fe(CN)_6$.</td><td rowspan="2">PRECIPITATE: Dark coloured, V_2S_4 or V_2S_5. Confirm vanadium.</td><td>FILTRATE: $H_3PO_4(WO_3)_{12}$. Remove PO_4 with $Mg(NO_3)_2$ and NH_4OH. Concentrate, add dil. HNO_3 and boil.</td></tr>
<tr><td>PRECIPITATE: Yellow H_2WO_4. Confirm Tungsten.</td></tr>
</table>

Section 12. Nickel Group.—This group, isolated as given in Section 10 and possibly containing rare earth elements, is analysed as indicated in Table 6.

Section 13. Zirconium Group.—The first peroxide precipitate in Section 10 may, in addition to In, Zr, and Ti, also contain rare earths and minor quantities of Zn, Co, and Ni. To it is added any rare earth precipitate from the nickel group and the whole dissolved in HCl and the solution evaporated nearly to dryness. To the residue is added 2 c.c. H_2O, $\frac{1}{2}$–2 c.c. of $27N$-HF and 1 c.c. of $6N$-HCl, and the mixture warmed on the water bath, the precipitated rare earth and indium fluorides being then removed and examined by Section 14.

Indium is also found in the filtrate and, together with any Ni, Co, and Zn, is removed by nearly neutralising and then passing in H_2S. Indium is confirmed by dissolving the sulphide in HCl, precipitating $In(OH)_3$ with excess ammonia, dissolving this in HCl, and again depositing the yellow In_2S_3. Zn, Co, and Ni are not tested for.

The fluoride filtrate containing Zr and Ti is fumed with H_2SO_4, diluted, H_2O_2 added, and any residue is removed. An orange solution indicates Ti. To this is added $1N$-Na_2HPO_4—white precipitate after standing $=$ Zr. If now

TABLE 6.

<table>
<tr><td colspan="5">Dissolve in HCl; replace chlorides by nitrates and heat with HNO_3 and $KClO_3$.</td></tr>
<tr><td rowspan="6">PRECIPITATE: Black MnO_2.
Confirm Manganese.</td><td colspan="4">FILTRATE: Nitrates of Zn, Co, Ni, and Rare Earths. Add NH_4OH until alkaline, acidify with CH_3COOH and add 10 c c. of $3N$-$CH_3CO_2NH_4$. Pass in H_2S.</td></tr>
<tr><td colspan="3">PRECIPITATE: ZnS, CoS, NiS. Treat with cold $1N$-HCl.</td><td rowspan="5">FILTRATE: Rare earths. Expel H_2S, add NH_4OH, filter and reject filtrate.
PRECIPITATE. Rare earth hydroxides.
ADD to Zirconium group Section 13</td></tr>
<tr><td colspan="2">SOLUTION: $ZnCl_2$ and little $CoCl_2$ and $NiCl_2$. Add $NaOH$ and Na_2O_2.</td><td rowspan="2">RESIDUE:
CoS.
NiS.</td></tr>
<tr><td rowspan="3">FILTRATE: $NaHZnO_2$.
Confirm Zinc.</td><td>PRECIPITATE: $Co(OH)_2$, $Ni(OH)_2$</td></tr>
<tr><td colspan="2">Dissolve in HCl and $KClO_3$.</td></tr>
<tr><td colspan="2">SOLUTION. Evaporate, add CH_3COOH and KNO_2
PRECIPITATE = yellow $K_3Co(NO_2)_6$. Test for nickel in FILTRATE with dimethylglyoxime.</td></tr>
</table>

the orange filtrate is decolorised with Na_2SO_3, then, on standing, a white precipitate of $Ti(HPO_4)_2$ is formed

Section 14. Rare Earth Group.—As indicated above, this group is isolated as the fluorides together with those of scandium, thorium, and indium. Scandium is first removed by heating these fluorides with HF and NH_4F (HF+NH_4OH), soluble NH_4ScF_4 being formed and confirmed in the filtrate. The residual salts are *converted through the sulphates and hydroxides* to acetates, after which indium is separated as In_2S_3. Further analysis is carried out according to Table 7.

TABLE 7.

<table>
<tr><td colspan="5">Evaporate the filtrate, convert to nitrates and heat on steam bath with HNO_3 and powdered $KClO_3$. Add KIO_3 solution, cool, and filter.</td></tr>
<tr><td colspan="2">PRECIPITATE. $Th(IO_3)_4$, $Ce(IO_3)_4$. Heat with H_2O_2 and HNO_3 on steam bath; add KIO_3. Cool and filter.</td><td colspan="3">FILTRATE: Rare earth iodates. Add NH_4OH, filter, and dissolve precipitate in HCl. Evaporate and add 3 c c. of 50% K_2CO_3.</td></tr>
<tr><td>RESIDUE $Th(IO_3)_4$.
Evaporate with HCl and add H_2O_2.</td><td>SOLUTION. $Ce(IO_3)_3$.
Add NH_4OH and H_2O_2.</td><td rowspan="2">PRECIPITATE: Lanthanum subgroup. Also little of Yttrium subgroup</td><td colspan="2">FILTRATE: Yttrium subgroup and some Nd, Sm, Eu. Boil with HCl, add NH_4OH and filter. Dissolve precipitate in HCl, evaporate. Add $HCOOH$ (90%) and $HCOONH_4$.</td></tr>
<tr><td rowspan="2">PRECIPITATE: White, $ThO_2 \cdot H_2O_2$.</td><td rowspan="2">PRECIPITATE. Orange, $CeO_2 \cdot H_2O_2$.</td><td>PRECIPITATE: Nd, Sm, Eu. Add to La subgroup.</td><td>FILTRATE: Yttrium subgroup.</td></tr>
<tr><td colspan="3">For further analysis of these groups, see original treatise (p 554)</td></tr>
</table>

Section 15. The Alkaline Earth Group.—The filtrate after the separation of the nickel and rare earth groups by means of NH_4OH and $(NH_4)_2S$ (*see* Section 10) contains the alkaline earth and alkali groups together with ammonium salts added during the analysis. The latter are removed by evaporation and gentle ignition, this operation being repeated after moistening the residue with $3N$-NH_4Cl. The final product is dissolved in water, filtered if necessary, and the alkaline earth metals precipitated with $6N$-$(NH_4)_2CO_3$ and an equal volume of alcohol. The carbonates of Ba, Sr, Ca, and Mg are filtered after ½ hour and examined according to Table 8.

TABLE 8.

<table>
<tr><td colspan="5">Dissolve in $CH_3{\cdot}COOH$; concentrate, dilute, and add $CH_3{\cdot}CO_2{\cdot}NH_4$ and K_2CrO_4.</td></tr>
<tr><td rowspan="5">PRECIPITATE: $BaCrO_4$.
Confirm Barium.</td><td colspan="4">FILTRATE: Add NH_4OH, warm, and add 15 c.c. EtOH.</td></tr>
<tr><td colspan="2">PRECIPITATE: $SrCrO_4$, $CaCrO_4$. Boil with NH_4 carbonate and K oxalate.</td><td colspan="2">FILTRATE: Ca and Mg salts. Add K oxalate.</td></tr>
<tr><td colspan="2">RESIDUE: $SrCO_3$, CaC_2O_4. Treat with $CH_3{\cdot}COOH$.</td><td>PRECIPITATE: CaC_2O_4, (MgC_2O_4). Treat with H_2SO_4.</td><td rowspan="2">FILTRATE: Mg salts.
Add Na_2HPO_4 and NH_4OH.</td></tr>
<tr><td>SOLUTION: Sr acetate. Add Na_2SO_4.</td><td rowspan="2">RESIDUE: CaC_2O_4.</td><td>SOLUTION: $CaSO_4$, $(MgSO_4)$. Add EtOH.</td></tr>
<tr><td>PRECIPITATE: $SrSO_4$.</td><td>PRECIPITATE: $CaSO_4$.</td><td>PRECIPITATE: $Mg(NH_4)PO_4$.</td></tr>
</table>

Section 16. The Alkali Group.—The filtrate remaining after the removal of the preceding group is evaporated, ignited to volatilise ammonium salts, and the residue dissolved in water. This solution is now treated with lead nitrate to convert any sulphates to nitrates and, after filtering, any excess of Pb is precipitated with H_2S. The filtrate containing only alkali nitrates or chlorides is cautiously evaporated to fuming with 1–5 c.c. of $9N$-$HClO_4$, cooled, and rinsed into a flask with a volume of alcohol equal to four times that of the $HClO_4$ used above. The flask is stoppered, shaken occasionally during 15 minutes, and the precipitated perchlorates of K, Rb, or Cs filtered off. In the filtrate sodium is separated from lithium by saturating with HCl gas and the precipitated NaCl is confirmed as the triple sodium magnesium uranyl acetate. The filtrate after the removal of NaCl is at once diluted with one-quarter to one-third its volume of water and cautiously heated on a steam-bath until the volume is equal to that of the perchloric acid originally added. The liquor is cooled and conc. HNO_3 is *cautiously* added drop by drop until action ceases, after which a further 1 c.c. is dropped in. The *solution* is again *cautiously* heated on the bath for ¼ hour when an additional ½ c.c. of HNO_3 is added. Heating is now carefully continued on a gauze until perchloric acid is expelled and the residue is gently ignited. 3 c.c. of 95% alcohol and 2 drops of NH_4OH (D=·880) are added, any residue filtered off, and the warmed filtrate is treated with 2 drops of $\frac{1}{2}N$-Na_2HPO_4. White precipitate after shaking$=Li_3PO_4$.

Note.—The removal of perchloric acid must be carried out as given above and the operator should be protected from any risks of explosion.

For the further analysis of the precipitated perchlorates of K, Rb, and Cs, it is necessary to obtain these as nitrites and this is accomplished by converting into the cobaltinitrites by digesting with $Na_3Co(CN)_6$ and a little acetic acid saturated with $NaNO_2$. The residue is transferred to a basin, moistened with $9N$-$NaNO_2$, evaporated, and gently ignited until effervescence ceases. The resulting nitrites are taken up in water, filtered from cobalt oxides, and the filtrate examined by Table 9 p. 564.

EXAMINATION FOR ACIDS.

Although it is not practicable to separate acidic radicals into a limited number of groups each with its appropriate group reagent, yet the analytical reactions for these radicals may be divided into (i) preliminary tests made on the original solution or material, and (ii) systematic tests applied to suitably prepared solutions. These reactions may be conveniently performed in the following order:

I. PRELIMINARY TESTS (compare dry reactions).

1. Original substance or solution is warmed with dilute *hydrochloric or sulphuric acid*. A gas is evolved, carbon dioxide turning lime water milky=*carbonates*; sulphur dioxide=*sulphites*;

TABLE 9.

<table>
<tr><td colspan="4">Solution of KNO_2, $RbNO_2$, $CsNO_2$ (with $NaNO_2$). Make acid with $CH_3{\cdot}COOH$, filter if necessary, and add $Bi(NO_3)_3$ (saturated solution in $6N$-$CH_3{\cdot}COOH$).</td></tr>
<tr><td>FILTRATE: $KNO_2(NaNO_2)$. Add $Co(NO_3)_2$.</td><td colspan="3">PRECIPITATE: Yellow $Rb_2NaBi(NO_2)_6$. $Cs_2NaBi(NO_2)_6$. Dissolve in HCl and add $SbCl_3$.</td></tr>
<tr><td rowspan="3">PRECIPITATE: Yellow, $K_2NaCo(NO_2)_6$.</td><td rowspan="3">PRECIPITATE: $3CsCl{\cdot}2SbCl_3$.</td><td colspan="2">FILTRATE: $RbCl$, $CsCl$, ($BiCl_3$, $SbCl_3$). Remove Bi and Sb with H_2S. Filter.</td></tr>
<tr><td colspan="2">FILTRATE: $RbCl$, $CsCl$. Evaporate and add NaH tartrate.</td></tr>
<tr><td>PRECIPITATE: RbH Tartrate.</td><td>FILTRATE: $CsCl$. Confirm with silicotungstic acid.
White precipitate, Cs Silicotungstate.</td></tr>
</table>

hydrogen sulphide, blackening lead acetate paper=*sulphides* (not all); nitrous fumes=*nitrites*; hydrogen cyanide, odour of bitter almonds=*cyanides*; chlorine oxides=*chlorites*.

2. *Original substance or solution warmed* slowly with strong solution of sodium dichromate slightly acidified, carbon dioxide evolved confirms *carbonate* in presence of sulphite.

3 *Addition of cold concentrated sulphuric acid*, carbon monoxide evolved, blue flame=*formate*.

4. Heating with concentrated sulphuric acid The foregoing gases (1, 2, and 3) may be evolved and also the following:

(*a*) Colourless Gases.—Fuming acid gas etching glass=*fluoride*; fuming acid gas not etching=*chloride*; odour of vinegar=*acetate*; carbon monoxide, blue flame=*formate, ferrocyanide*; carbon monoxide and dioxide=*oxalate*; sulphur dioxide and sulphur sublimate=*thiosulphate*.

(*b*) Coloured Gases.—Orange vapour, bromine, and sulphur dioxide=*bromide*; violet vapour and sulphur dioxide=*iodide*; nitrous fumes=*nitrite, nitrate*; oxides of carbon and sulphur with charring=*tartrate, citrate, malate*; yellow explosive chlorine oxide=*chlorate*.

5. Heating with alcohol and concentrated sulphuric acid—green flame=*borate*. Before performing this test, chlorates must be decomposed by igniting the original substance in order to avoid an explosion.

6. Heating with concentrated sulphuric acid and sand—a colourless gas (SiF_4), giving a gelatinous precipitate on moistened rod confirms *fluoride*.

II. SYSTEMATIC TESTS.—Before testing a solution for acids, boil with excess of pure sodium carbonate to remove most of the heavy metals (uranium, thorium, and certain of the other rare earth metals are not precipitated at this stage). The filtration from the carbonate precipitate is neutralised with nitric acid.

1. *Barium chloride* in neutral solution yields (*a*) a white precipitate insoluble in hydrochloric acid=*sulphate, silicofluoride*; (*b*) a white precipitate soluble in hydrochloric acid=*sulphite, phosphate, oxalate, borate, fluoride, silicate, tartrate*, (*c*) yellow precipitate soluble in hydrochloric acid=*chromate*

2. *Calcium chloride* added in excess to the *neutral solution causes gradual deposition of a* white precipitate, (*a*) insoluble in acetic acid=*oxalate* (*sulphate* in strong solutions); (*b*) soluble in acetic acid=*phosphate, borate*, and other acidic radicals precipitated by barium chloride. *Calcium tartrate*, when washed, becomes soluble in caustic potash, but is reprecipitated on diluting and boiling. Filtrate from the foregoing precipitate in the cold is boiled for some time, a white precipitate=*citrate* (*malate* in strong solutions). The solution filtered hot from this precipitate is cooled and mixed with excess of alcohol, a white precipitate=*succinate, malate*.

3. *Silver nitrate* in neutral solution yields:

(*a*) A precipitate soluble in nitric acid—

(1) White=*oxalate* (somewhat sparingly soluble in nitric acid); *borate* (formed only in strong solution; $Ag_3BO_3+3H_2O=H_3BO_3+3AgOH$); *tartrate, benzoate*, and many other organic carboxylic acids to be identified by special tests.

(2) Yellow=*phosphate, arsenite*.

(3) Brick-red=*arsenate*.

(4) Dark red=*chromate*.

(*b*) A precipitate insoluble in nitric acid. Soluble in ammonia: white=*chloride* (hypochlorite), *cyanide, thiocyanate*; yellowish-white=*bromide*; orange-red=*ferricyanide*; white =*ferrocyanide* (sparingly soluble). Insoluble in ammonia: yellow=*iodide*; black=*sulphide*.

4. *Ferric chloride* in neutral solution yields—

(*a*) A coloration·deep red, giving a precipitate on boiling=*acetate, formate*; blood red, no precipitate on boiling = *thiocyanate*. Violet = *salicylate*,

thiosulphate (fugitive); bluish-black=*tannate, gallate.* Greenish-brown=*ferricyanide* (dark blue precipitate on adding stannous chloride).

(*b*) A precipitate: buff=*benzoate, carbonate*; reddish-brown=*succinate*; white=*phosphate*; black=*sulphide*; bluish or greenish black= *tannate, gallate.*

Sulphur Acids.—(1) Detect *sulphate* by barium chloride and *sulphide* by lead acetate. Make a portion of the solution slightly alkaline with caustic potash or soda, add zinc sulphate in large excess, and filter. Test one part of filtrate for *thiosulphate* by hydrochloric acid (SO_2 evolved and sulphur deposited) or transitory violet coloration with ferric chloride; to the other part add, successively, acetic acid till faintly acid, sodium nitroprusside in small amount, and potassium ferrocyanide: a pink precipitate indicates a *sulphite.* (2) Separation of soluble sulphates, sulphites, thiosulphates, and sulphides in neutral solution. Precipitate *sulphide* as CdS, PbS, or ZnS by adding cadmium carbonate or lead carbonate sludge or zinc chloride solution (yellow, brownish-black, or white precipitate). To filtrate add strontium nitrate and leave for 12 hours; the co-precipitated strontium *sulphate* and *sulphite* are separated by hydrochloric acid, the latter dissolving with evolution of sulphur dioxide. The filtrate from the two strontium precipitates contains *thiosulphate,* which on decomposition with strong hydrochloric acid evolves sulphur dioxide and deposits sulphur.

Chloride, Bromide, and Iodide.—(1) Place mixture in a small distilling flask connected with a bulbed V-tube containing starch paste and surrounded by cold water. Add water and ferric sulphate solution (ferric alum) to the flask and heat to boiling. In presence of iodide the starch paste becomes blue. This process is continued till all iodine is expelled, then add a little solid permanganate, connect with V-tube containing chloroform or carbon tetrachloride, and boil again. In presence of a bromide the organic solvent becomes brown. Repeat the treatment with permanganate until all bromine is expelled. Filter the residue and test filtrate for chloride. (2) After iodide has been detected by sodium nitrite in acidified solution

$$(2HI+2HNO_2=2H_2O+2NO+I_2)$$

a portion of the solution is evaporated to dryness with sodium carbonate and fused with ten times its weight of potassium dichromate until the iodine is completely expelled. The residue is then distilled with strong sulphuric acid from a small retort. Part of the distillate is shaken with chloroform or carbon disulphide when the organic solvent becomes brown in presence of bromine (bromide). The remainder of the distillate is neutralised with ammonia and tested for chromate by acidifying with acetic acid and adding lead acetate. The presence of chromate in the neutralised distillate is due to a volatile chromium compound (CrO_2Cl_2), which in turn indicates *chloride* in the original solution.

(3) A neutral solution of the three halides is treated with potassium iodate and dilute acetic acid: as iodine is liberated ($5HI+HIO_3=3I_2+3H_2O$) more iodate is added and the solution boiled till all iodine is removed. The solution is then mixed with half its volume of 5*N*-nitric acid, bromine is evolved, and the solution boiled till colourless. A little potassium iodide is added to destroy any excess of iodate; the solution again boiled till colourless when an equal volume of strong nitric acid and a few drops of sodium nitrite are added successively with further boiling. A white precipitate on addition of silver nitrate indicates a chloride. If thiocyanic acid is present the test for iodide must be made in a small portion of the original solution, adding sodium acetate as well as acetic acid to depress the dissociation of the latter.

Other acid radicals must be detected by special tests. Iodides, ferrocyanides, and ferricyanides must be removed before testing for nitrates. For this purpose the original substance is treated with excess of a mixture of cupric and ferrous sulphates. Excess of copper and iron is removed from the filtrate by boiling and adding slight excess of pure caustic soda when the nitrate tests may be applied to the final filtrates.

To remove bromine and iodine the original substance is acidified with dilute sulphuric acid and boiled with potassium permanganate until the liquid retains a faint pink tinge; the filtrate may then be examined for nitrate or chloride.

Hypochlorites and nitrites are destroyed by boiling with dilute sulphuric acid. The latter salts may also be decomposed by boiling with strong aqueous ammonium chloride:

$$NaNO_2+NH_4Cl=NaCl+2H_2O+N_2$$

SPECIAL REACTIONS.

Whereas the analytical ideal of one specific test for each element is far from being realised, yet the continued discovery of new and increasingly sensitive reagents, especially organic ones, has brought much nearer the possibility of attaining such a goal. The reactions given below are only a selection of the most characteristic, and additional tests may be found in the section devoted to micro-analysis. The elements have been arranged according to the groups of the periodic classification.

Lithium.—*Ammonium fluoride,* white precipitate (LiF), more complete in presence of ammonia or alcohol. *Sodium phosphate,* white precipitate (Li_3PO_4) soluble in hydrochloric acid and reprecipitated by ammonia on boiling. *Sodium arsenate* in ammoniacal-alcoholic solution, pale pink precipitate, Li_3AsO_4 (Gaspar y Arnal, Ann. Chim. Analyt. 1933 [ii], **15**, 193). Lithium chloride, unlike other alkali chlorides, is soluble in many organic media such as *n*- and *iso*-butyl alcohols, amyl alcohol, and diethylene dioxide (dioxan). Lithium (and sodium) perchlorate is soluble in alcohol or a mixture (1:1) of ethyl acetate and *n*-butyl alcohol (Moser and Schutt, Monatsh. 1929, **51**, 23; Brown and Reedy, Ind. Eng. Chem. (Anal.), 1930, **2**, 304; Sinka, Z. anal. Chem. 1930, **80**, 430; Yagoda, J. Amer. Chem. Soc. 1932, **54**, 984).

Sodium.—The most satisfactory method for detecting sodium, or, indeed, any alkali metal, is spectroscopically. All sodium salts are more or less soluble and precipitation methods presuppose a considerable concentration of the element. The most delicate reagent is *zinc, magnesium,* or *nickel uranyl acetate*, the zinc triple salt is obtained as a yellow precipitate with excess of reagent ($NaZn[(UO_2)_3(OAc)_9]$) (Kolthoff and others, *1927–1936*). *Bismuth nitrate* in 50% *potassium nitrite*, containing *cæsium nitrite*, yellow crystalline precipitate ($5Bi(NO_2)_3.9CsNO_2.6NaNO_2$). *Potassium pyroantimonate* and *dihydroxytartaric acid* give colourless precipitates of $Na_2H_2Sb_2O_7.6H_2O$ and $Na_2C_4H_4O_8$ respectively.

Potassium.—*Platinichloric acid*, yellow crystalline precipitate (K_2PtCl_6) more complete in the presence of alcohol. *Sodium cobaltinitrite* in acetic acid, yellow precipitate

$$R_3[Co(NO_2)_6], \text{ where } R=Na+K);$$

ammonia gives a similar precipitate. *Perchloric acid*, white crystalline precipitate. *Cobalt nitrate* in 80% methyl alcohol and *sodium thiosulphate* (38% aqueous solution), blue precipitate in neutral solutions (Celsi, Anal. Farm. Bioquim. 1933, 4, 55) *Sodium 6 chloro-5 nitrotoluene-3-sulphonate*; *sodium 1 amino-β naphthol-6-sulphonate* (*eikonogen*), *iokaonic acid* and *sodium picrate* give characteristic precipitates with potassium.

Rubidium.—*Platinichloric acid*, yellow crystalline precipitate (K, Cs, and NH_4 interfere) *Perchloric acid*, white crystalline precipitate, *sodium cobaltinitrite*, yellow precipitate. *Palladous chloride* and *auric chloride* in dilute hydrochloric acid, brown precipitate ($Rb_2AuPdCl_7$) (Tananaev, Z. anal. Chem. 1932, 88, 343) *Potassium bismuth iodide* ($KBiI_4$), no precipitate (distinction from Cs and Tl).

Cæsium.—Cæsium behaves like rubidium and potassium towards *platinichloric acid, perchloric acid, sodium cobaltinitrite. Potassium bismuth iodide*, brown precipitate *Silicotungstic acid* in 6*N*-hydrochloric acid, white precipitate, $Cs_4[SiO_4(WO_3)_{12}]$ (distinction from Rb). *Auric bromide* and *platinic bromide*, black precipitate (Rb interferes only in concentrations greater than 2%) (Burkser and Kutschment, J Appl. Chem. Russ, 1936, 9, 145) *Stannic chloride* in hydrochloric acid, white precipitate, $Cs_2[SnCl_6]$, *antimonious chloride* in hydrochloric acid, white precipitate, $Cs_3[SbCl_6]$

Alone of alkali carbonates, cæsium carbonate, Cs_2CO_3, *is soluble in absolute ethyl alcohol*, but in presence of Rb_2CO_3, a mixture of the two carbonates passes into solution.

Copper.—Cupric salts. *Hydrogen sulphide*, black precipitate almost insoluble in dilute sulphuric acid or ammonium sulphide; soluble in nitric acid or potassium cyanide. *Ammonia*, blue precipitate, soluble in excess reagent to deep-blue solution. *Potassium ferrocyanide*, chocolate-brown precipitate, insoluble in dilute acids. *Potassium iodide*, whitish-brown precipitate ($Cu_2I_2+I_2$). *Pyridine+ammonium thiocyanate*, blue complex $[Cu(C_5NH_5)_2(SCN)_2]$ soluble in chloroform (Spacu's reaction). Benzidine or tolidine gives similar precipitates. *Gallic acid+ammonium thiocyanate*, colourless turbidity or precipitate. (Ag, Pb, Bi interfere.) Similar results are obtained using tannic acid, catechol, or quinol (Spacu, Z. anal. Chem. 1925, 67, 31; Fleming, Analyst, 1924, 49, 275; Falcioli, Giorn. Chim. Appl 1921, 3, 354). *Benzoin monoxime* (in alcoholic solution) and in presence of tartaric acid, sap green precipitate. This is said to be specific for copper (Feigl, Österr. Chem. Ztg., 1923, 26, 75). *Rubeanic acid* in alcoholic solution, black precipitate. This test is sensitive to 1 in $2\frac{1}{2}$ millions, but nickel and cobalt interfere (Pr. Rây and R. M. Ray, J. Ind. Chem. Soc. 1926, 3, 118).

Cuprous Salts.—The cuprous halides are sparingly soluble in water, but dissolve in concentrated hydrochloric acid *Sodium hydroxide*, yellow precipitate, becoming red on boiling (Cu_2O) *Potassium ferrocyanide*, white precipitate becoming brownish red on exposure to air. p-*Dimethylaminobenzalrhodanine* (saturated alcoholic solution), red precipitate or colour (silver and mercury interfere) (Funakoshi, Mem. Coll Sci Kyoto, 1929, 12, 155).

Silver.—*Hydrochloric acid*, white precipitate insoluble in nitric acid, soluble in ammonia, potassium cyanide, or sodium thiosulphate. Silver bromide and iodide show a decreasing solubility in ammonia. *Potassium chromate*, dark red precipitate (Ag_2CrO_4), soluble in mineral acids and decomposed by caustic alkalis. p *Dimethylaminobenzalrhodanine*, red precipitate in neutral or slightly acid solutions (halogens Hg and Cu interfere, gold gives a colour, but not in the presence of potassium cyanide) 1·8-*Dihydroxynaphthalene* 3 6 *disulphonic acid* (chromotrope acid), black precipitate (iron gives intense green colour, but this disappears in acid solution).

Gold.—Auric chloride may be extracted from solutions containing slight excess of hydrochloric acid with ethyl acetate; any mercuric chloride which may also be extracted is removed by shaking with 3*N*-ammonium chloride *Hydrogen sulphide*, black precipitate (Au_2S_3) from cold solution, soluble in ammonium sulphide; from hot solutions the metal is precipitated. *Reducing agents*, brown or purplish precipitates of the metal. *Hydrogen peroxide* in very dilute alkaline solution: the liberated gold has a beautiful blue shimmer.

Beryllium.—*Ammonia or alkali hydroxides*, white precipitate $[Be(OH)_2]$, soluble in excess of alkali hydroxide but reprecipitated on boiling. *Ethylamine*, same white precipitate, insoluble in *excess of reagent (difference from aluminium). Ammonium sulphide* also precipitates the hydroxide. Unlike aluminium hydroxide, beryllium hydroxide is insoluble in boiling sodium bicarbonate. *Quinalizarin* in alkaline solution, the violet colour of the reagent becomes blue; magnesium gives a similar blue lake discharged, however, by bromine water (Fischer, Z. anal. Chem. 1928, 73, 54)

Beryllium may be separated from many metals by precipitating the latter with tannin under slightly acid conditions (solution buffered with ammonium acetate); beryllium is only precipitated in neutral solution (Moser and Singer. Monatsh 1927, 48, 673).

Another separation is based on the solubility of the basic acetate, $BeO,3Be(C_2H_3O_2)_2$, in dry chloroform. p-*Nitrobenzeneazoorcinol* (0·025% solution in $NaOH$), orange-red colour. Zinc, nickel, cobalt, copper, cadmium, and silver interfere, but not in the presence of potassium cyanide. Magnesium gives a brownish-yellow colour (Komarovsky and Poluektov, Mikrochem. 1934, **14**, 315).

Magnesium.—*Ammonia*, white precipitate, $Mg(OH)_2$; no precipitate if sufficient ammonium chloride is present. *Sodium phosphate, ammonia, and ammonium chloride*, white precipitate becoming crystalline,

$$Mg(NH_4)PO_4,6H_2O\,;$$

the precipitate appears only slowly from dilute solutions. *Sodium hypoiodite* in neutral solution, red-brown precipitate (Al and excess ammonium salts interfere). *Quinalizarin* (0·01% alcoholic solution) added to the test solution followed by sodium hydroxide gives a blue precipitate stable after acidifying with hydrochloric acid (Be and Al interfere; tartaric acid prevents the interference of Al). *Titan yellow* (0·1% solution), colour changed from orange to red by magnesium hydroxide (Al, Sn, and Bi interfere).

Calcium.—*Ammonium carbonate*, white precipitate ($CaCO_3$), soluble in acids. *Sulphuric acid*, white precipitate, $CaSO_4$, from strong solutions, soluble in ammoniacal ammonium sulphate. *Ammonium oxalate*, white precipitate (CaC_2O_4); insoluble in oxalic or acetic acid, soluble in hydrochloric acid. *Sodium salt of the osazone of dihydroxytartaric acid*, white precipitate. This test is sufficiently delicate to detect calcium in slightly hard waters such as 1 part of London tap water in 80 parts of distilled water. In such cases the test is best made on a blackened watch glass or spotting tile and using a crystal of the solid osazone. *Ammonium ferrocyanide*, white crystalline precipitate,

$$Ca(NH_4)_2[Fe(CN)_6].$$

Potassium ferrocyanide also gives a precipitate, $Ca_2[Fe(CN)_6]$.

Strontium.—*Ammonium carbonate*, white precipitate ($SrCO_3$) soluble in acids. *Sulphuric acid or soluble sulphates*, $SrSO_4$, white precipitate, forming slowly in the cold, more quickly on heating; the precipitate is insoluble in ammoniacal ammonium sulphate. *Potassium chromate*, yellow precipitate, $SrCrO_4$, only in concentrated solutions. *Ammonium oxalate*, white precipitate (SrC_2O_4), insoluble in acetic acid, soluble in hydrochloric acid.

Barium.—*Ammonium carbonate*, white precipitate ($BaCO_3$), soluble in dilute hydrochloric acid. *Sulphuric acid or soluble sulphates*, immediate white precipitate ($BaSO_4$) insoluble in ammoniacal ammonium sulphate. *Potassium chromate*, yellow precipitate ($BaCrO_4$), insoluble in acetic acid (distinction from Sr). *Ammonium oxalate*, white precipitate, BaC_2O_4, nearly insoluble in cold acetic acid, soluble in hydrochloric acid. *Tetrahydroxybenzoquinone* (hot saturated aqueous solution), deep red precipitate insoluble in dilute hydrochloric acid. (Lead gives a precipitate soluble in acetic acid; strontium gives a brown colour bleached by dilute hydrochloric acid).

Zinc.—*Ammonium sulphide*, white precipitate (ZnS), insoluble in acetic acid or alkalis, soluble in dilute mineral acids. *Alkali hydroxide or ammonia*, white precipitate, soluble in excess of reagent. *Potassium ferrocyanide*, white precipitate, $Zn_3K_2[Fe(CN)_6]_2$, insoluble in dilute acetic acid. *Potassium ferricyanide*, orange precipitate, soluble in dilute hydrochloric acid or ammonia. This test is more distinctive in presence of certain aromatic amines, such as diphenylamine or diethylaniline (Cone and Cady, J. Amer. Chem. Soc. 1927, **49**, 2214). *Diphenylthiocarbazone* (Dithizone) (0·002% solution in carbon tetrachloride), a slightly acid, sodium acetate buffered, solution of zinc salt when shaken with this reagent converts the original green colour to purple-red. Ni, Co, and Cd do not interfere under these conditions, but Cu, Hg, Ag, Au, Pd, and $Sn^{\cdot\cdot}$ should be removed (Fischer and Leopoldi, Z. anal. Chem. 1934, **97**, 385). *Borneolglycuronic acid*, a reagent prepared from the urine of dogs fed with borneol, is said to be specific for zinc in absence of cadmium; a white precipitate $(C_{16}H_{25}O_7)_2Zn,2H_2O$ is obtained (Quick, Ind. Eng. Chem. Anal. 1933, **5**, 26).

Cadmium.—*Hydrogen sulphide*, yellow precipitate, insoluble in alkali or ammonium sulphides and potassium cyanide; soluble in hot dilute mineral acids. *Caustic alkalis* or *ammonia*, white precipitate, $Cd(OH)_2$, soluble in excess of ammonia. *Diphenylcarbazide* (saturated solution in 90% alcohol) in neutral solution, blue-violet colour on adding ammonia; the interfering action of copper is prevented by adding potassium thiocyanate and potassium iodide (Feigl, Z. anal. Chem. 1923, **62**, 369). *Thiosinamine* in presence of sodium hydroxide, yellow precipitate on heating (Gutzeit, Helv. Chim. Acta, 1929, **12**, 713).

Mercury. Mercurous Salts.—*Soluble chlorides*, white precipitate (Hg_2Cl_2), insoluble in most non-oxidising solvents; blackened with ammonia; *alkali hydroxides*, black precipitate. *Potassium iodide*, greenish-yellow precipitate (Hg_2I_2), soluble in excess with separation of mercury. *Stannous chloride*, grey precipitate (Hg). *Diphenylcarbazide* (1% alcoholic solution) to faintly acid test solution (p_H about 3·8)—blue-violet colour soluble in chloroform or benzene.

Mercuric Salts.—*Hydrogen sulphide*, whitish-yellow precipitate, rapidly becoming red and then black (HgS); insoluble in ammonium sulphide or nitric acid, soluble in sodium sulphide (Na_2HgS_2) or *aqua regia*. *Alkali hydroxides*, in excess, yellow precipitate. *Potassium iodide*, scarlet precipitate, soluble in excess. *Stannous chloride*, white precipitate rapidly turning grey with excess. This test is more distinctive in the presence of aniline (Tananaev, Z. anorg. Chem. 1924, **133**, 372). *Diphenylcarbazide*, as for mercurous, but colour is insoluble in benzene.

Boron. Borates.—*Silver nitrate*, white precipitate ($AgBO_2$) from moderately concentrated solutions, soluble in nitric acid or ammonia; in dilute solutions or on warming

brown silver oxide is formed. *Alcohol* and *strong sulphuric acid*, green edged flame on burning the alcohol; methyl alcohol is more sensitive than ethanol (copper and barium interfere). *Turmeric paper* dipped into a solution of borate acidified with dilute hydrochloric acid and dried, orange to red colour becoming blue black with alkalis.

Perborates.—Tests for perborates resemble those for hydrogen peroxide, a yellow colour is formed with *titanium trichloride*, while aqueous *chrome alum* gives blue perchromic acid soluble in ether.

Aluminium.—*Ammonia*, white gelatinous precipitate, $Al(OH)_3$; *alkali hydroxides* give the same precipitate soluble in excess of the reagent but reprecipitated by ammonium chloride. Soluble *sulphides* and *carbonates* also form the hydroxide with liberation of hydrogen sulphide and carbon dioxide respectively. *Aluminon* (aurintricarboxylic acid), red lake with dilute acetic acid test solution, colour due to excess of reagent is minimised by adding ammonia and ammonium carbonate. (Fe and reducing agents interfere.) *Morin* (tetrahydroxy-flavanol), a saturated solution of the dye yields a green fluorescence with dilute, neutral, or acetate-buffered solutions containing aluminium (Eegriwe, Z anal Chem 1929, **76**, 440).

Gallium.—*Ammonia* or *alkali hydroxides*, white precipitate, $Ga(OH)_3$, soluble in excess; precipitation is hindered by tartrates *Soluble carbonates* give a white precipitate of basic carbonate soluble in ammonium carbonate *Potassium ferrocyanide*, white precipitate, insoluble in hydrochloric acid (up to 3 5N). The sensitivity of this test is increased by adding manganous chloride and an oxidising agent ($KBrO_3$), when a red brown colour or precipitate is obtained (Poluektov, Mikrochem 1936, **19**, 248). *Alizarin* in presence of *ammonia* and *ammonium chloride*, bright red lake.

These tests should be carried out after extraction of gallium chloride with ether, removal of gallium hydroxide with sodium hydroxide, and precipitation with 8 hydroxyquinoline. The gallium complex is then decomposed with dilute acid (Poluektov, l c).

Indium.—*Ammonia*, white precipitate, $In(OH)_3$, only slightly soluble in excess. *Alkali hydroxides*, similar precipitate peptised by excess of reagent, but coagulated on boiling or standing. *Soluble carbonates*, white precipitate of basic carbonate, soluble in ammonium carbonate. *Hydrogen sulphide*, yellow precipitate (In_2S_3) in neutral or acetic acid solution; soluble in sodium sulphide or dilute mineral acids. *Potassium ferrocyanide*, white precipitate more soluble in hydrochloric acid than the gallium compound. *Aluminon*, red lake, insoluble in ammonia but decomposed by ammonium carbonate (distinction from Sc and Al).

Thallium. Thallous Salts.—*Soluble chlorides*, white precipitate (TlCl), slightly soluble in cold water, more soluble in hot. *Potassium iodide*, yellow precipitate only slightly soluble in sodium thiosulphate (distinction from Pb). *Ammonium sulphide*, black precipitate, (Tl_2S), easily oxidised in air; the precipitation with hydrogen sulphide from neutral solution is incomplete. *Potassium chromate*, yellow precipitate, (Tl_2CrO_4). *Sodium cobaltinitrite*, pale red crystalline precipitate.

Thallic Salts.—*Soluble chlorides*, no precipitate *Potassium iodide*, brown precipitate (probably mixture of TlI, TlI_2 and TlI_3). *Alkali hydroxides or ammonia*, brown precipitate ($Tl(OH)_3$).

Thallic salts give blue colorations with *benzidine acetate*, *a-naphthol* or *dimethyl p-phenylenediamine*; other oxidising agents produce similar colours

Rare Earth Metals.—These belong to the third analytical group and are precipitated by ammonia as hydroxides insoluble in alkali hydroxides; tartrates and citrates hinder precipitation. They form neutral or basic carbonates with ammonium carbonate, the yttrium earth carbonates being soluble in excess. They also form insoluble phosphates.

Minerals containing the rare earths may in some cases be decomposed with hydrochloric acid, others yield to sulphuric acid, while a few require alkali fusion Alternatively, hydrofluoric acid may be used and is advantageous in that rare earth (and thorium) fluorides are insoluble in excess of this acid whereas most other fluorides dissolve The commonest method of separating this group is as oxalates which are insoluble in excess of oxalic acid, in this way any zirconium, aluminium, iron, or hexavalent uranium may be removed Thorium, which generally accompanies the rare earths, may be separated by means of hydrogen peroxide, ammonium sebacate, boiling with sodium thiosulphate or by taking advantage of the solubility of its oxalate in ammonium oxalate The two last methods also serve to remove scandium

With the exception of cerium the rare earths can only be separated from each other by tedious fractionation following upon the division into the yttrium and cerium groups. This is accomplished by the use of saturated potassium or sodium sulphate when the cerium group is precipitated as double sulphates insoluble in alkali sulphate The separation is not sharp and must follow the lines of a fractionation.

Cerium is removed by oxidising with potassium bromate in neutral solution when the ceric salt hydrolyses and a basic salt is precipitated It is also separated as the double ammonium nitrate $Ce(NO_3)_4\,2(NH_4)NO_3$, which is sparingly soluble in nitric acid. Alternatively cerium (and thorium) may be precipitated as iodates.

Traces of cerium may be detected by the yellow colour given with hydrogen peroxide in alkaline solution, by the intense blue colour developed by ceric salts with benzidine acetate, or by the scarlet colour given with methylene blue.

Lanthanum may be detected by the blue adsorption complex of its basic acetate with iodine (*see* ACETIC ACID).

Carbon.—Carbon is detected by its appearance, by its inactivity towards the usual analytical reagents, and by its combustion in air or oxygen to form carbon dioxide. This oxidation may also be accomplished with potassium dichromate and sulphuric acid.

Carbon Monoxide.—A colourless, poisonous gas which readily burns in air with a blue flame forming the dioxide. It is detected by the liberation of iodine from iodine pentoxide, by its power to reduce palladous chloride to palladium, and by its alteration of the absorption spectrum of blood.

Carbon Dioxide (*see* CARBONATES).

Cyanogen.—Cyanogen is a colourless gas with the odour of peach kernels; it burns with a purple flame. If the dry gas is passed into an alcoholic solution of sodium hydrosulphide, the solution becomes dark red and on acidification rubeanic acid is precipitated. A dilute alcoholic solution of this acid gives a violet precipitate with ammoniacal nickel salts.

The gas may also be detected by passing it into a solution made up of 2 c.c. saturated picric acid, 18 c.c. of alcohol, and 5 c.c. of 15% potassium hydroxide, when a purple-red colour forms which soon turns brown.

Carbon Disulphide.—Colourless liquid with characteristic odour giving a white compound with phenylhydrazine and a red crystalline compound with triethylphosphine. It dissolves in sodium sulphide solution forming sodium thiocarbonate (Na_2CS_3), which yields a brown precipitate with silver nitrate soluble in excess thiocarbonate; lead nitrate gives a red precipitate quickly becoming black.

Shaken with ammonia (0·880) the upper layer contains ammonium dithiocarbamate, which gives a black precipitate with silver nitrate in neutral or alkaline solution. The liquid assumes a red colour discharged by acetic acid (Gutzeit, Helv. Chim. Acta, 1929, 12, 713).

Small quantities may be detected by test papers made with a solution of a copper or cobalt salt in excess of dimethylamine or pyridine which develop brown colorations. Hydrogen sulphide interferes but not in the presence of cyanide.

Cyanides.—*Dilute acids,* hydrogen cyanide evolved (sometimes only on heating); absorption of the gas in yellow ammonium sulphide and treatment of solution with ferric chloride gives a blood-red colour. *Silver nitrate,* white precipitate, insoluble in cold dilute nitric acid, soluble in ammonia or excess of cyanide. *Prussian blue test.* To the solution is added successively caustic soda, ferrous sulphate, a few drops of ferric chloride and heated. On adding hydrochloric acid in excess the presence of cyanide is denoted by a blue colour or precipitate.

Cyanates.—*Dilute acid,* carbon dioxide is evolved and an ammonium salt formed. *Silver nitrate,* white precipitate ($AgCNO$), soluble in dilute nitric acid or ammonia. *Cobalt acetate,* blue colour, $K_2[Co(CNO)_4]$, becoming pink on dilution; the blue colour is more stable in ether.

Thiocyanates.—*Silver nitrate,* white precipitate insoluble in dilute nitric acid, soluble in ammonia. *Ferric chloride,* blood-red colour discharged by mercuric chloride. *Cobalt chloride,* blue colour soluble in ether and amyl alcohol. *a-Naphthol* (20% alcoholic solution), and concentrated sulphuric acid, green colour becoming violet on shaking. *Copper sulphate,* black precipitate, $Cu(CNS)_2$, becoming white $Cu_2(CNS)_2$ on adding sulphurous acid.

Ferrocyanides.—Heated with dilute sulphuric acid they evolve hydrogen cyanide, while with strong acid carbon monoxide is liberated. *Silver nitrate,* white precipitate insoluble in nitric acid, sparingly soluble in ammonia; soluble in potassium cyanide. *Copper sulphate,* chocolate-brown precipitate. *Ferric chloride,* dark blue precipitate. *Ferrous sulphate,* white precipitate rapidly becoming blue. *Ammonium molybdate* in dilute hydrochloric acid solution, brown precipitate of molybdenyl ferrocyanide. (Separation from ferricyanides.)

Ferricyanides.—*Silver nitrate,* orange precipitate insoluble in nitric acid, soluble in ammonia. *Ferric chloride,* greenish-brown colour. *Ferrous sulphate,* dark blue precipitate. *Cadmium nitrate,* orange precipitate.

Ferrocyanides may be separated from ferricyanides or thiocyanates by precipitating as thorium ferrocyanide in dilute acid solution or as the molybdenyl compound. Ferricyanides and thiocyanates can be separated by precipitating the former as the cadmium salt.

Nitroprussides.—Heated with hydrochloric acid they give hydrogen cyanide and ferric chloride. *Alkali sulphides,* purple colour destroyed by alkalis. *Sodium amalgam* in alkaline solution gives sodium ferrocyanide and ammonia; in acid solution it forms "Prussian Blue." Zinc nitroprusside gives a rose colour with *sulphur dioxide.*

Carbonates and Bicarbonates.—*Dilute acids,* evolution of carbon dioxide which turns lime or baryta water turbid. *Barium chloride,* white precipitate. *Mercuric chloride,* red precipitate of basic carbonate, bicarbonates give a yellowish opalescence only. *Calcium sulphate,* immediate white precipitate with carbonate; bicarbonates give same precipitate on standing or addition of ammonia.

Formates.—*Concentrated sulphuric acid,* evolution of carbon monoxide without blackening. *Silver nitrate,* white precipitate in strong solutions; rapidly darkens precipitating metallic silver. *Mercuric chloride,* white precipitate turning grey with excess of formate. *Ferric chloride,* dark red colour depositing brown precipitate on boiling. The red colour is discharged by mineral acids.

Free formic acid gives a reddish-yellow colour when warmed with strong sodium bisulphite solution.

Acetates.—*Concentrated sulphuric acid,* evolution of acetic acid on heating; addition of ethyl alcohol gives the characteristic odour of ethyl acetate. *Ferric chloride* gives an analogous reaction to that with formates. *Arsenious oxide* heated with acetates, yields cacodyl-oxide, $As_2(CH_3)_4O$, with nauseating odour. *Lanthanum nitrate* and ammonia, white basic lanthanum acetate which with iodine in potassium iodide forms a blue adsorption complex similar to "starch iodide." Propionates give a similar reaction, but other organic acids only depress the sensitivity of the test (Krüger and Tschirch, Ber. 1929, 62 [B], 2776; Chem.-Ztg. 1930, 54, 42).

Oxalates.—*Concentrated sulphuric acid,* evolution of carbon monoxide and dioxide.

Potassium permanganate and dilute sulphuric acid, decolourised on adding drop by drop to warm test solution. *Calcium chloride*, white precipitate, insoluble in acetic acid, soluble in dilute mineral acids. *Resorcinol* (concentrated solution), followed by concentrated sulphuric acid down the side of the tube, blue ring at the interface on gently shaking. *Ammonium metavanadate* (0·5% solution) and a few drops of hydrogen peroxide give a ruby red colour with oxalates (other reducing agents interfere).

Succinates.—*Calcium or barium chloride*, white precipitate if not too dilute. *Silver nitrate*, white precipitate, soluble in nitric acid. *Ferric chloride*, reddish-brown precipitate of basic ferric succinate, soluble in dilute acids, decomposed by ammonia.

The dry substance heated with resorcinol and 1–2 drops of concentrated sulphuric acid yields a green fluorescent solution on extraction with alkali.

Malates.—*Calcium chloride*, white precipitate only in strong, hot solutions or on adding alcohol. *Lead acetate*, white precipitate ($PbC_4H_4O_5$), *melting in hot water, soluble in warm acetic* acid. *Silver nitrate*, white precipitate becoming grey on boiling.

Strong solutions of the acid containing a little ferrous sulphate give an intense red colour when *treated carefully at 0° with hydrogen peroxide*. Addition of ferric salts intensifies the colour.

Tartrates.—*Calcium chloride*. White precipitate soluble in dilute mineral and acetic acids, soluble in sodium hydroxide after washing but reprecipitated on boiling *Silver nitrate*, white precipitate soluble in nitric acid and ammonia; the solution in the minimal quantity of the latter reagents deposits a silver mirror on warming. *Potassium acetate* and *acetic acid*, white precipitate more complete on warming.

Oxidation with hydrogen peroxide in the presence of ferrous sulphate (*see* Malates) produces a deep violet or blue colour on adding excess of caustic soda.

Citrates.—*Calcium chloride*, white precipitate of calcium citrate formed more readily on boiling or adding a little sodium hydroxide. *Cadmium chloride*, gelatinous white precipitate insoluble in hot water, soluble in acetic acid (difference from tartrate). *Mercuric sulphate* in acid solution followed by *potassium permanganate*, white turbidity due to mercuric acetonedicarboxylate (halogens interfere). *Silver nitrate*, white precipitate soluble in ammonia but ammoniacal solution not readily reduced on warming.

Benzoates.—*Mineral acids*, white crystalline precipitate of benzoic acid (m.p 121°), sparingly soluble in cold water, readily so in alcohol or ether. *Ferric chloride*, reddish brown precipitate decolourised by hydrochloric acid to white benzoic acid. *Silver nitrate*, white precipitate soluble in hot water. *Soda lime*, evolution of benzene on dry distillation with this reagent.

Salicylates.—*Mineral acids*, white crystalline precipitate of salicylic acid (m.p. 159°). *Ferric chloride*, purple or violet colour even with dilute solutions; the colour is discharged by mineral acids and by organic acids or alkalis if present in excess. *Silver nitrate*, white precipitate soluble in hot water. *Strong sulphuric acid* and *methyl alcohol*, characteristic odour of methyl salicylate (oil of wintergreen) on heating. *Bromine water*, white precipitate yielding phenol with sodium amalgam. *Soda lime*, odour of phenol on dry distillation.

Gallic Acid.—*Ferric chloride*, bluish-black precipitate soluble in excess to green solution. *Gelatin* or *albumin*, no precipitate (distinction from tannic acid). *Ammoniacal silver nitrate*, silver mirror even in the cold. *Lime water* in excess, blue precipitate becoming dark on standing. *Potassium cyanide* in dilute solution, rose colour fading quickly but reappearing on shaking in air. *Alkali hydroxides*, greenish coloration becoming brownish red with excess.

Tannic Acid.—*Ferric chloride*, bluish black precipitate or coloration. *Gelatin* or *albumin*, immediate white precipitate. *Lime water*, greyish white precipitate. *Potassium cyanide*, yellowish-red colour not fading appreciably.

Reactions with *ammoniacal silver nitrate* or *alkali hydroxides* are similar to those with gallic acid.

Pyrogallol.—*Ferric chloride*, reddish-yellow colour. *Concentrated hydrochloric acid* with *formaldehyde* (2–3 drops), white precipitate rapidly changing through red to purple. *Silver nitrate*, deposits silver even from cold neutral *reagent solution*. *Alkali hydroxides*, yellow solution rapidly becoming dark brown.

Phenol.—*Ferric chloride*, violet colour discharged by acids and alkalis *Bromine water*, white precipitate of tribromophenol, excess of reagent forms tribromophenol bromide which when washed well liberates iodine from potassium iodide *Sodium hypochlorite* and *ammonia*, blue colour on warming, changed to bright red with hydrochloric acid. *Strong sulphuric acid* and a crystal of *sodium nitrite*, green or blue solution becoming red on pouring into water; excess of alkali reconverts the colour to blue.

Uric Acid.—The alkali salts reduce *silver-nitrate* in the cold and Fehling's solution on boiling. *Soda lime*, dry distillation leads to evolution of ammonia and formation of sodium cyanide which can be detected by the Prussian blue test. *Nitric acid*, followed by careful evaporation of solution to dryness, orange residue developing an intense violet colour with ammonia and a blue colour with alkali hydroxides (Murexide test).

Silicon.—*Silicates*. Most silicates are insoluble in water; those that are soluble and a few insoluble ones are decomposed by acids depositing silicic acid; others require fusion with sodium and potassium carbonates, acidification of the melt with hydrochloric acid yields silicic acid which when evaporated to dryness with excess acid furnishes silica (SiO_2) insoluble in all acids except hydrofluoric. *Fluorides* and *strong sulphuric acid*, evolution of silicon tetrafluoride detected by forming a white gelatinous film on a wet glass rod. *Calcium chloride* or *silver nitrate*, white precipitate with soluble silicates; the precipitates are easily decomposed by acids.

Traces of silicic acid are identified after bringing into solution by adding excess of ammonium molybdate and careful acidification. The

yellow-green colour of the silicomolybdic acid formed $\{H_8[Si(Mo_2O_7)_6]xH_2O\}$ may be intensified by adding a reducing agent such as sodium sulphite (in which case the previous acidification is made with acetic acid) or strongly alkaline sodium stannite; in both cases a deep blue colour is formed (Oberhauser and Bergheim, Z. anorg. Chem. 1929, **178**, 381; Isaac, Bull. Soc. Chim. biol. 1924, **6**, 157). If benzidine be used as reducing agent, the blue colour can be extracted with amyl alcohol (phosphates interfere) (Feigl and Krumholz, Ber. 1929, **62**, [B], 1138).

Silicofluorides.—Silicofluorides decompose on heating liberating silicon fluoride and leaving a residue of metallic fluoride. Heated with strong sulphuric acid they give silicon fluoride and hydrogen fluoride. *Barium chloride*, white precipitate ($BaSiF_6$) nearly insoluble in dilute hydrochloric acid. *Potassium chloride*, white precipitate from moderately strong solutions. *Thorium nitrate*, white precipitate.

Germanium.—The outstanding feature of *this element is the ready volatility of its chloride*, whereby it may be separated from all elements except tervalent arsenic and selenium. Small quantities may be detected by electrolysis of alkaline solutions with nickel electrodes or reduction with sodium amalgam and passing the germanium hydrides formed through a heated tube when a brownish or metallic stain is produced; pentavalent arsenic does not interfere (Coase, Analyst, 1934, **59**, 462, 747).

Germanates with ammonium molybdate in dilute nitric acid give blue colours with benzidine acetate or Mohr's salt and sodium acetate; silicates and phosphates interfere (Komarovsky and Poluektov, Mikrochem. 1935, **18**, 66; Z. anal. Chem. 1936, **105**, 23).

Germanates in molybdate-nitric acid solution if evaporated to dryness, extracted with water and filtered give with cold lead chloride solution a pale yellow crystalline precipitate of lead germanomolybdate. *Hydrogen sulphide* in strong acid solution (5*N*-), white precipitate soluble in alkalis, ammonia and alkali sulphides; no precipitate in the presence of excess of hydrogen fluoride (distinction from As). *Alkalis* or *ammonia*, partial white precipitate only from concentrated acid solutions and soluble in excess.

Tin. Stannous Salts.—*Hydrogen sulphide*, chocolate-brown precipitate (SnS), soluble in ammonium polysulphide, insoluble in dilute hydrochloric acid, ammonia or ammonium carbonate. *Caustic alkalis*, white precipitate soluble in excess; this stannite solution reduces strongly ammoniacal silver nitrate to metallic silver in the cold ($As^{\cdots}$ and $Sb^{\cdots}$ solutions only reduce on boiling). *Sodium nitroprusside* in alkaline solution, greyish-red colour turning blue with hydrochloric acid. *Mercuric chloride*, white precipitate becoming grey with excess of test solution. 4-*Chloro* (or *Methyl*)-1:2-*dimercaptobenzene* (0·2% solution in sodium hydroxide) added to a stannous solution in dilute hydrochloric acid ($\not>$15%) gives a pink or red colour on warming. Bismuth gives an easily distinguishable brick red precipitate with this reagent (Clark, Analyst, 1936, **60**, 242).

Stannic Salts.—*Hydrogen sulphide*, dirty yellow precipitate (SnS_2), soluble in colourless ammonium sulphide or ammonia, partially soluble in ammonium carbonate; insoluble in dilute hydrochloric acid. *Mercuric chloride*, no precipitate. Anhydrous stannic oxide, when fused on charcoal, with fusion mixture ($KNaCO_3$) and sulphur, gives a soluble melt containing alkali thiostannate, $KNaSnS_3$, from which acid precipitates yellow stannic sulphide.

Lead.—*Soluble chlorides*, white precipitate ($PbCl_2$) insoluble in ammonia, soluble in hot water. *Hydrogen sulphide*, black precipitate, insoluble in dilute hydrochloric acid, soluble in hot dilute nitric acid. *Sulphuric acid*, white precipitate, soluble in ammonium acetate or tartrate. *Potassium chromate*, yellow precipitate insoluble in acetic acid, soluble in alkali hydroxides. *Diphenylthiocarbazide* (in carbon tetrachloride) shaken with lead solutions containing 5% potassium cyanide, gives a brick-red coloration (this test is specific for lead and *detects 0·1 microg. in 0·05 c.c.).*

Oxidising agents form brown lead peroxide which gives a blue colour with tetramethyl-*p*-diaminodiphenylmethane or benzidine acetate (other peroxides interfere). Alternatively, the lead peroxide may be deposited anodically and then tested when only manganese interferes (Danckwort and Jurgens, Arch. Pharm. 1928, **266**, 367, 374; Necke and Müller, Angew. Chem. 1935, **48**, 259).

Titanium.—Titanium is usually found as hydrated titania in the ammonia precipitate provided sufficient acid has been present during earlier treatment to prevent hydrolysis. *Alkali hydroxides* or *carbonates, ammonia* or *ammonium sulphide*, white precipitate of orthotitanic acid in the cold; soluble in dilute acids, slightly soluble in alkalis; hot precipitation produces metatitanic acid (H_2TiO_3), which is insoluble; precipitation is hindered by tartrates. *Sodium thiosulphate* or *acetate*, white precipitate on boiling. *Potassium ferrocyanide*, reddish-yellow precipitate with Ti^{iv}; lower valencies give dark brown precipitates. *Reducing agents* give violet, blue, or green colours. *Hydrogen peroxide* in weak acid solutions, yellow to red colour; fluorides, phosphates, excess of alkali salts, $Fe^{\cdots}$, $Cr^{\cdots}$, Mo and V interfere. *Tannin* in neutral oxalate or tartrate solutions, deep orange precipitate on warming, soluble in mineral acids and oxalic acid.

Many phenols give red or yellow colours with quadrivalent titanium; thus thymol in 80% sulphuric acid and in the absence of tungsten gives a yellow to dark red colour.

Zirconium and Hafnium.—These two elements cannot, at present, be differentiated by qualitative analysis. *Alkali hydroxides, ammonia, ammonium sulphide*, white gelatinous precipitate, insoluble in excess; soluble in dilute mineral acids (avoid sulphuric) when precipitated cold, soluble only in concentrated acids when produced from hot solutions. (Tartrates interfere.) *Ammonium oxalate*, white precipitate soluble in excess of reagent (distinction from Al and Be); this solution also gives no precipitate with hydrochloric acid (distinction from

Th). *Potassium sulphate* in cold concentrated solution, white precipitate,

$$[Zr(Hf)O(SO_4)_2]K_2.3H_2O,$$

insoluble in excess. *Sodium phosphate*, white precipitate insoluble in moderately strong *mineral acids (separation from most other elements)*. *Hydrogen peroxide*, white milky precipitate liberating chlorine when warmed with hydrochloric acid. *Tannin*, no precipitate from neutral oxalate solution. *Alizarin 3-sulphonic acid*, violet colour becoming yellow with traces of fluoride (Basart, Z. anorg. Chem. 1926, 152, 213).

Thorium.—*Alkali hydroxides or ammonia*, white gelatinous precipitate $(Th(OH)_4)$ insoluble in excess. *Alkali and ammonium carbonates*, white basic carbonate soluble in excess. *Oxalic acid*, white precipitate insoluble in dilute mineral and oxalic acids. *Ammonium oxalate*, same precipitate, soluble in excess but reprecipitated by dilute mineral acids *Hydrogen peroxide* in neutral or slightly acid solution, complete precipitation of thorium peroxide (separation from Ce). *Potassium iodate* in nitric acid solution, white precipitate $(Th(IO_3)_4)$ (distinction from Ce and Sc) *Soluble fluorides*, white precipitate (ThF_4), (separation from Sc) *Sebacic acid* with neutral solution, white precipitate (separation from rare earth metals).

Nitrogen. Hydrazoic Acid.—*Ferric chloride*, blood-red colour disappearing on boiling with deposition of ferric hydroxide. It is distinguishable from the colour with thiocyanates in being discharged by dilute mineral acids and being less easily affected by mercuric chloride. *Iodine* and one drop of *sodium thiosulphate*, evolution of nitrogen. No reaction takes place between soluble azides and iodine except in the presence of thiosulphates, sulphides, or thiocyanates. *Copper sulphate*, red-brown precipitate; *silver nitrate*, white precipitate, insoluble in cold dilute nitric acid, soluble in ammonia.

Hydrazine.—Powerful reducing agent precipitating mercury, silver, gold, etc., from solution, *benzaldehyde* in acid or alkaline solution, yellow precipitate of benzaldazine,

$$C_6H_5CH\ N\ N\ CHC_6H_5.$$

Ethyl nitrite and *alkali*, hydrazine is oxidised to hydrazoic acid which can be detected with ferric chloride. *Copper sulphate* with hydrazine hydrate, blue precipitate.

Hydroxylamine.—The reducing action of hydroxylamine is not so great as that of hydrazine. *Copper sulphate* in ammoniacal solution, red cuprous oxide. *Benzoyl chloride* and sodium acetate, benzhydroxamic acid is formed which gives a violet colour with ferric chloride. *Ammonium polysulphide* boiled with test solution until sulphur appears and 2 c.c. strong ammonia and 2 c.c. alcohol added, purple red colour (hydrazine does not interfere).

Solutions of hydroxylamine treated with a fragment of sodium nitroprusside and a little sodium hydroxide give a magenta colour when heated quickly to 100°.

Ammonia and Ammonium Salts.—Ammonia is a colourless gas with a characteristic odour and an alkaline reaction in the presence of moisture. It gives copious white fumes with hydrogen chloride. It may be detected by the purple colour given with tetramethyldiaminodiphenylmethane or the carmine red colour with logwood extract. A very sensitive test is the silver mirror which it produces on a drop of silver nitrate solution containing 3% formaldehyde. Ammonium salts are volatile and liberate ammonia when heated with lime or caustic alkalis. *Platinichloric acid*, yellow crystalline precipitate slightly soluble in water. *Nessler's reagent* (K_2HgI_4 and KOH), yellow solution to brown precipitate. *Phenol* (4% solution) and dilute *sodium hypochlorite*, blue colour.

Ammonium salts, like those of potassium, give a precipitate with sodium cobaltinitrite, but they differ from this alkali metal in giving no precipitate with perchloric acid or fluosilicic acid.

Nitrates.—*Sulphuric acid*, evolves nitric acid on heating; if metallic copper be added then brown *oxides of nitrogen are liberated. Ferrous sulphate and strong sulphuric acid*, the neutral test solution is mixed with ferrous sulphate and the acid then poured *carefully* down the side of the tube, dark purplish brown ring is formed at the interface (iodides and bromides interfere). *Brucine* in strong sulphuric acid, red colour (oxidising agents must be absent) *Diphenylamine* or *diphenylbenzidine* in sulphuric acid, blue colour. *Nitron acetate*, white precipitate.

Nitrites.—*Silver nitrate*, white precipitate from strong solutions *Starch-iodide* and *acetic acid*, blue colour. *Safranine T* (0 03% solution) and dilute mineral acid, violet to blue colour. *Potassium ferrocyanide* and acetic acid, greenish-yellow colour (distinction from nitrate). *Dimethyl-α naphthylamine* (0 5% solution in 4*N*-acetic acid) gives a rose red colour with a nitrite in 15% methanol. Dilute acetic acid solution of *sulphanilic acid* with *α naphthylamine* forms a deep red solution (Ilosvay test). A more permanent colour is obtained if dimethyl-α-naphthylamine is used (Germuth, Ind. Eng. Chem. Anal. 1929, 1, 28).

Phosphorus.—This element may be detected by its luminescence, or by conversion to phosphine (PH_3) on boiling with sodium hydroxide. The phosphine is detected by silver nitrate or mercuric chloride test papers which turn black or yellow respectively.

Phosphates.—*Calcium* or *barium chloride*, white precipitate soluble in dilute mineral acid *Ammonium molybdate* in dilute nitric acid, yellow precipitate on warming, soluble in ammonia and excess of alkaline phosphate. A sensitive reagent, producing a precipitate in the cold (distinction from arsenate), may be made by dissolving 140 g. of ammonium molybdate in a mixture of 200 c.c. of ammonia (d=0 880) and 200 c.c. of water. To this solution is added slowly, with stirring, 1,500 c.c. of nitric acid (d=1·23) and the mixture allowed to stand overnight in a warm place. The clear solution is decanted and diluted with an equal volume of water. *Magnesium sulphate, ammonium chloride,*

and *ammonia*, white crystalline precipitate, $Mg(NH_4)PO_4,6H_2O$, soluble in mineral acids. Metaphosphates give no precipitate, while the pyrophosphate precipitate is soluble in excess of magnesium sulphate. *Silver nitrate*, yellow precipitate, soluble in nitric acid and ammonia. Meta- and pyro-phosphates give white precipitates. The meta- acid may be distinguished from the other two by its ability to coagulate albumin and by forming a brownish-yellow precipitate with luteo cobaltic chloride in acetic acid solution. The pyro- acid gives an orange precipitate soluble in acetic acid.

Phosphites.—*Barium chloride*, white precipitate ($BaHPO_3$) soluble in hydrochloric acid. *Silver nitrate*, white precipitate, rapidly darkening with formation of the metal especially in the presence of ammonia and heat. *Mercuric chloride*, white precipitate rapidly becoming grey. *Copper sulphate*, pale blue precipitate.

Phosphites are easily oxidised to phosphates or reduced with nascent hydrogen to phosphine.

Hypophosphites.—Heated alone they evolve phosphine, while in solution they possess powerful reducing properties. Heated with excess of alkali they evolve hydrogen. *Barium chloride*, white precipitate only from strong solutions. *Copper sulphate*, red precipitate (Cu_2H_2), giving metallic copper and hydrogen on heating to 100°.

Silver, mercury, arsenic, and bismuth salts are reduced to the metal. Hypophosphites decolorise iodine in the presence of sulphuric acid while phosphites only do so in the presence of sodium acetate.

Arsenic.—Arsenic compounds reduced with zinc and dilute sulphuric acid form volatile arsine (AsH_3), which is decomposed by heat giving a black deposit of arsenic soluble in aqueous hypochlorites. A similar stain produced with antimony is insoluble in hypochlorites (Marsh's Test). Arsine is also produced on reduction with zinc (or aluminium) and caustic soda and forms yellow to brown stains on mercuric chloride test paper or a brown to black spot on silver nitrate paper (Gutzeit-Fleitmann test). *Hydrogen sulphide*, yellow precipitate, insoluble in hydrochloric acid, soluble in ammonium sulphide or carbonate. *Phosphorus trichloride*, brown precipitate (As) (distinction from Sb). *Metallic copper* and dilute hydrochloric acid, steel grey deposit on warming. Heated in an open tube the deposit gives a white crystalline sublimate (As_4O_6). *Stannous chloride* in hot concentrated hydrochloric acid, brown colour or precipitate (As); a trace of mercuric chloride increases the sensitivity (Bettendorff's test).

Arsenites.—*Silver nitrate* to solution kept neutral with ammonia, yellow precipitate soluble in nitric acid and ammonia, insoluble in 0·5–1·5*N*-sodium hydroxide. *Ammoniacal copper sulphate*, green precipitate soluble in excess of ammonia; hot sodium hydroxide turns the precipitate red (Cu_2O).

Arsenates.—*Silver nitrate* in neutral solution, brick red precipitate, soluble in nitric acid and ammonia. *Magnesia mixture*, white crystalline precipitate, $Mg(NH_4)AsO_4,6H_2O$. *Copper sulphate* in neutral solution, blue precipitate becoming black with hot caustic soda (CuO). *Ammonium molybdate* in sulphuric acid followed by stannous chloride, blue colour (silicates, phosphates, and germanates interfere).

Antimony.—*Hydrogen sulphide*, orange precipitate, soluble in ammonium sulphide, sodium hydroxide, and hot strong hydrochloric acid. *Water* in excess and in presence of chlorides, white precipitate (SbOCl) soluble in tartaric acid and in mineral acids. *Zinc* in contact with *platinum*, black stain on the platinum which dissolves in nitric acid or ammonium sulphide. *Pyrocatechol* with antimony chloride in a solution first neutralised and then made acid with tartaric acid, white precipitate (this test is said to be specific). *Pyridine* and *potassium iodide* in strongly acid solution, yellow colour. *Antipyrine* and *potassium iodide*, yellow precipitate.

Bismuth.—*Hydrogen sulphide*, brown precipitate insoluble in ammonium sulphide, soluble in nitric acid. *Water* in excess and in presence of chlorides, white precipitate (BiOCl), insoluble in tartaric acid, soluble in mineral acids. *Alkali hydroxides* or *ammonia*, white precipitate soluble in mineral acids. Stannous chloride (3 drops of 20% solution) in *potassium hydroxide* (5 c.c. of 10% solution) and in presence of tartaric acid, black precipitate. *Pyrogallol* to weak hydrochloric acid solution (0·1*N*-), yellow crystalline precipitate on boiling (Sb alone interferes, giving a white precipitate).

Like antimony, bismuth gives delicate colour reactions or precipitates with potassium iodide and certain organic bases; *e.g.* quinine sulphate (orange-red colour) and antipyrine (brick-red precipitate). The most delicate test is that given with potassium iodide and tetra-acetyl-ammonium hydroxide, an intense red colour develops which is soluble in benzene (Girard and Fourneau, Compt. rend. 1925, **181**, 610).

Bismuth compounds heated on charcoal with potassium iodide and sulphur give a crimson-red incrustation.

Vanadium (as vanadates).—*Mild reducing agents* (H_2S, SO_2, etc.) in acid solutions, blue vanadyl salts. *Strong reducing agents* ($Zn+H_2SO_4$), progressive colour changes of blue to green to violet. *Ammonium sulphide*, deep brown solution, depositing a brown precipitate (V_2S_5) when acidified. *Potassium ferrocyanide* in acid solution, green flocculent precipitate. *Hydrogen peroxide* in acid solution, reddish-brown colour insoluble in ether and unaffected by phosphoric acid (distinction from Fe) or hydrogen fluoride (distinction from Ti). *Tannin* with hot acetic acid solution, blue-black precipitate. *Strychnine sulphate* in strong sulphuric acid, blue-violet colour becoming rose-red.

Niobium (as niobates).—*Mineral acids*, white precipitate of niobic acid, sparingly soluble in excess. *Zinc dust* and *acid*, blue colour (distinction from Ta). *Hydrogen fluoride* and *potassium fluoride*, no precipitate even on boiling. *Tannin*, orange-red precipitate. *Codeine*, pink colour.

Tantalum (as tantalates).—*Mineral acids*, white precipitate of tantalic acid soluble in excess. *Hydrogen fluoride* and *potassium fluoride*, white crystalline precipitate, K_2TaF_7, on boiling. *Tannin*, pale yellow precipitate. *Codeine*, faint green colour.

Oxygen.—Free oxygen is detected by its power to rekindle a glowing splint, by forming brown nitrogen peroxide with nitric oxide, and by the deep red colour given with alkaline pyrocatechol and ferrous sulphate.

Ozone.—Ozone possesses a characteristic odour and manifests the usual properties of a strong oxidant, but does not decolourise acidified permanganate. *Benzidine test paper* (made from a saturated alcoholic solution), brown colour; nitrous fumes give blue colour; chlorine, blue and then red-brown; hydrogen peroxide does not interfere. *Tetramethyl p diaminodiphenylmethane test paper*, violet colour; nitrous fumes give straw-yellow and chlorine and bromine blue colours. Hydrogen peroxide does not interfere. Ozone also destroys the fluorescence of fluorescein.

Hydrogen Peroxide.—*Potassium iodide* and *starch*, blue "starch iodide" *Ammoniacal silver nitrate*, grey precipitate (Ag). The most usual tests are the formation of blue perchromic acid (*see* Cr) or yellow pertitanic acid (*see* Ti). A highly sensitive test with a reagent made from 1% alcoholic o *tolidine*

$$(NH_2\cdot C_7H_6\, C_7H_6\, NH_2),$$

1% *ferrous sulphate* and acetate buffer at p_H 4, a blue colour is developed with $2\,5\times10^{-8}$ g H_2O_2 (Kulberg and Matveev, J. Appl Chem. Russ. 1936, 9, 754)

Sulphur.—This non metal burns in air forming sulphur dioxide, it is soluble in carbon disulphide, forms sulphate with oxidising agents, and thiocyanate when heated with alkali cyanides. With fuming sulphuric acid (SO_3) sulphur gives blue solutions (*cf* selenium and tellurium).

Hydrogen Sulphide and Metallic Sulphides.—Hydrogen sulphide is easily detected by its odour, by blackening lead acetate paper, or by the orange colour produced with tartar emetic test paper

Most sulphides evolve hydrogen sulphide when heated with hydrochloric acid. *Sodium nitroprusside* in alkaline solution, intense purple colour. *Sodium azide* and *iodine*, evolution of nitrogen on warming Insoluble sulphides give this reaction also, but thiosulphates and thiocyanates interfere.

Hyposulphites (hydrosulphites) —Detection of these salts (such as $Na_2S_2O_4$) depends on their strong reducing action and their decomposition in acid media to form hydrogen sulphide. *Ammoniacal copper sulphate*, copper mirror. *Cupric chloride*, white precipitate becoming black on warming

$$(Cu_2Cl_2 \rightarrow Cu + Cu_2S).$$

Cadmium sulphate in dilute acid, yellow precipitate on boiling. *Titanic oxide* in sulphuric acid solution, intense red colour gradually fading through yellow to colourless.

Thiosulphates.—*Mineral acids*, white precipitate of sulphur and evolution of sulphur dioxide. *Silver nitrate*, white precipitate, ($Ag_2S_2O_3$), passing through brown to black (Ag_2S) on warming; silver thiosulphate dissolves in excess of thiosulphate. *Iodine solution*, decolourised and the solution then gives no precipitate with barium chloride. *Sodium azide* and *iodine*, liberation of nitrogen. Jelley and Clark (Brit. J. Phot. 1929, 76, 714) use this test as follows: 1 drop of the test solution in a small crucible is treated with 1 drop of starch iodide and 1 drop of 2% sodium azide. If the liquid contains more than $0\,0_3 1N$-thiosulphate the colour disappears. *Ferric chloride*, transient violet colour:

$$Fe_2(S_2O_3)_3 = FeS_2O_3 + FeS_4O_6.$$

Thionates ($M_2S_xO_6$, where x=2 to 5).—All thionates are decomposed by heat, yielding generally sulphates, sulphur dioxide, and, except with dithionates, sulphur. Reducing agents (Zn and acid) liberate hydrogen sulphide on warming; oxidants form sulphates.

Barium chloride, no precipitate except after oxidation. *Mercurous nitrate*, black precipitate with trithionic acid; yellow precipitates with the tetra- and penta- acids. *Ammoniacal silver nitrate*, with trithionates—no brown colour in cold but black Ag_2S on warming; with tetrathionates—brown colour on warming; with pentathionates—immediate brown colour developing to black on standing. *Caustic soda*, precipitate of sulphur with pentathionic acid *Dilute hydrochloric acid*, evolution of sulphur dioxide with trithionates

Sulphur Dioxide and Sulphites.—Sulphur dioxide is detected by its odour, its decolorising action on acid permanganate or iodine and by turning acid dichromate test paper green A rose red colour is also given when zinc nitroprusside is exposed first to ammonia and then to sulphur dioxide,

$$(NH_4)_4[SO_3,NO\ Fe\ (CN)_5]$$

Hydrochloric acid on sulphites, evolution of sulphur dioxide but no sulphur precipitated. *Barium chloride*, no precipitate in the presence of hydrochloric acid. *Iodic acid* and starch, a blue "starch iodide" is obtained with traces of sulphite; excess of the latter destroys the colour. *Fast Blue R (Oxazine)* (0·01% solution), added in drops to sulphite solution, a violet and then yellow colour (sulphides interfere).

Sulphates.—*Barium chloride and dilute hydrochloric acid*, white precipitate, insoluble in acids and alkalis. *Mercuric nitrate* (10% solution in 1% nitric acid), yellow crystalline precipitate on boiling ($HgSO_4\cdot 2HgO$). This test may be used for insoluble sulphates. *Barium rhodizonate*, decolorised by neutral or alkaline sulphates. This test is made on paper impregnated with fresh sodium rhodizonate solution followed by faintly acid barium chloride solution. The paper is used while still slightly damp.

Persulphates.—Powerful oxidising agents, they are converted into sulphates with reducing agents or on heating; in the latter case oxygen is evolved. *Barium chloride*, no precipitate except on reduction or heating. *Silver nitrate*, black precipitate (Ag_2O). *Benzidine acetate* in neutral or dilute acetic acid solution; blue colour (alkali peroxides, perborates, or hydrogen peroxide do not interfere; chromates, permanganates, ferricyanides, and hypohalites do). *Potassium permanganate*, no decoloration.

Selenium.—Like sulphur, selenium is converted on heating in air or oxygen into selenium dioxide which dissolves in water to form selenious acid. The same oxidation may be accomplished with nitric acid. Selenium is soluble in ammonium sulphide. Dissolved in strong sulphuric acid selenium gives green coloration rendered more sensitive on addition of codeine.

Selenides.—*Hydrochloric acid*, evolution of hydrogen selenide on warming; this gas is recognised by its odour and by the formation of a mirror under the conditions of the Marsh test for arsenic. If dissolved in water and air then passed through the solution, a red precipitate of selenium is obtained. Hydrogen selenide also gives a precipitate of sulphur and selenium with sulphites. *Metallic silver*, black satin stain with solution of selenides.

Selenites.—*Hydrogen sulphide* in dilute acid solution; lemon yellow precipitate ($Se+S$), soluble in ammonium sulphide; the precipitate becomes red on heating. *Reducing agents*, precipitate of red or black selenium. *Barium chloride*, white precipitate soluble in dilute hydrochloric acid. *Codeine phosphate* added to selenites in strong sulphuric acid, green or bluish-green colour (Fe interferes). *Magnesia mixture*, white precipitate insoluble in acids.

Selenates.—*Hydrogen sulphide*, no precipitate. Mild reducing agents have no effect on selenates. *Strong reducing agents*, red or black selenium. *Hydrochloric acid*, evolution of chlorine on boiling. *Barium chloride*, white precipitate ($BaSeO_4$) insoluble in cold dilute hydrochloric acid, dissolving on boiling.

Tellurium.—Tellurium closely resembles selenium in its reactions; the chief differences are listed below. With fuming sulphuric acid it gives a carmine solution. *Potassium cyanide* fused with tellurium forms soluble potassium telluride; its aqueous solution, when aerated, deposits the non-metal:

$$2K_2Te+2H_2O+O_2=4KOH+2Te$$

Under the same conditions selenium forms potassium selenocyanate, the solution of which is stable but gives selenium with acids:

$$KCNSe+HCl=KCl+HCN+Se$$

Inasmuch as $HCNS$ is stable to aqueous acids this cyanide fusion serves to separate the three elements of the sulphur family. *Hydrogen chloride*, white precipitate of H_2TeO_3 with tellurites. *Hydrogen sulphide* in acid solution, gives brown precipitate ($Te+S$), with tellurites and tellurates, the precipitate dissolves in ammonium sulphide. *Sulphur dioxide*, black precipitate (Te) with tellurites and tellurates except in strong hydrochloric acid solution, when no separation occurs even on boiling. *Potassium iodide* to acidified tellurite, a black precipitate, TeI_4, dissolving in excess to K_2TeI_6

Chromium. Chromic Salts.—*Alkali hydroxides* or *ammonia*, blue-green precipitate, $Cr(OH)_3$, soluble in dilute acids; the precipitate is soluble in excess alkali hydroxide to a green solution and partially soluble in excess ammonia to a pink solution; in both cases the hydroxide is reprecipitated on boiling. *Oxidising agents*, yellow solution of chromate. *Sodium phosphate*, green precipitate soluble in acetic acid, but reprecipitated on boiling. *Acid alizarin yellow RC.*, orange-coloured lake, stable to acids and ammonia.

Chromates and Dichromates.—*Reducing agents*, colour changes from yellow to green. *Lead acetate*, yellow precipitate, ($PbCrO_4$), insoluble in acetic acid. *Silver nitrate*, crimson-red precipitate, soluble in nitric acid and ammonia. *Hydrogen peroxide* in acid solution, deep blue evanescent colour, more stable if extracted with ether, amyl alcohol or ethyl acetate. *a-Naphthylamine*, violet-black colour. *Benzidine acetate*, blue colour (other oxidising agents interfere with this and the previous test). *Disodium salt of 1:8-dihydroxynaphthalene-3:6-disulphonic acid* in aqueous solution and in presence of phosphoric acid gives a red-brown colour.

Molybdenum (molybdates).—*Hydrogen sulphide*, reddish to brown colour in neutral or alkaline solutions; acid solutions are coloured blue followed by a brown precipitate (MoS_3) soluble in ammonium sulphide and nitric acid, insoluble in hydrochloric acid or boiling oxalic acid. *Potassium thiocyanate*, yellow colour changing to deep red with stannous chloride; this colour is soluble in ether and is not affected by phosphoric acid (distinction from $Fe^{\cdots}$). *Potassium xanthate* (alcoholic potash+carbon disulphide) in acetic acid, dark red colour soluble in ether or benzene (organic acids, Cu, Ni, Co, Fe, and $UO_2^{\cdot\cdot}$ interfere). *Sodium phosphate to nitric acid solution of molybdate*, yellow precipitate on warming, soluble in ammonia or excess reagent. *Phenylhydrazine* in acetic acid, red colour or precipitate. *Hydrogen peroxide* and *ammonia*, red-brown colour. *Sulphuric acid* solution of molybdate evaporated nearly to dryness develops a deep blue coloration.

Tungsten (tungstates).—*Hydrochloric acid*, white amorphous precipitate in the cold ($WO_3{\cdot}2H_2O$); changed to yellow on boiling ($WO_3{\cdot}H_2O$). Metatungstates give no precipitate except on boiling (phosphates and organic acids interfere). *Reducing agents*, blue colour (quinquivalent W). *Hydrogen sulphide* in acid solutions, no precipitate. *Ammonium sulphide*, no precipitate except after acidification, when brown WS_3 is deposited. *Rhodamine B* (0·001% solution) with an alkali tungstate acidified with hydrochloric acid, violet colour or fluorescence ($Hg^{\cdot\cdot}$, $Au^{\cdots}$, Sb, Bi, and Mo interfere).

Uranium.—Uranium salts are divisible mainly into two classes, the green uranous (U^4) salts, which are strong reducing agents, and the yellow uranyl compounds possessing a greenish fluorescence.

Uranous Salts.—*Ammonium sulphide*. Solution darkens rapidly and gives a black precipitate on warming. *Alkali hydroxides* or *ammonia*, pale green precipitate {$U(OH)_4$}, insoluble in excess; oxidises in air with colour change to brown (tartrates and carbonates hinder precipitation). *Alkali carbonates* or *bicarbonates*, pale green precipitate soluble in excess of bicarbonates or ammonium carbonate; easily

oxidised in air. *Potassium ferrocyanide,* yellowish-green precipitate gradually becoming brown. *Soluble fluorides,* precipitate of UOF_2. Uranous, but not uranyl, salts give a precipitate with cupferron.

Uranyl Salts.—*Ammonium sulphide,* brown precipitate (UO_2S), insoluble in excess, soluble in dilute acids and ammonium carbonate (distinction from Zn, Mn, Fe, etc). *Alkali hydroxides* or *ammonia,* yellow precipitates of diuranates, $M_2U_2O_7$ (hindered by tartrates, citrates, or peroxides), soluble in ammonium carbonate. *Potassium ferrocyanide,* deep red precipitate soluble in sodium hydroxide, ammonium carbonate, or dilute hydrochloric acid (distinction from $Cu^{\cdot\cdot}$). *Thiosinamine* in alkaline solution, yellow precipitate, this test is said to be specific in the absence of cadmium *Hydrogen peroxide,* pale yellow precipitate becoming deep yellow or red with carbonates (Cr, Ti, and V interfere). *Turmeric paper* with slightly acid test solution, brown colour darkening with sodium carbonate.

Fluorine.—A colourless, highly corrosive gas, it may be detected by its ability to etch glass. With silica it forms silicon tetrafluoride (*see* silicon); it liberates chlorine from hydrogen chloride.

Fluorides.—*Strong sulphuric acid* with fluorides in platinum or lead vessel, evolution of hydrogen fluoride detected by "etching" test. Addition of silica gives silicon tetrafluoride *Barium* or *calcium chloride,* white precipitate somewhat soluble in hydrochloric acid, soluble in ammonium chloride. *Silver nitrate,* no precipitate *Zirconium alizarin reagent.* the deep violet-red lake formed from zirconium nitrate or chloride with excess of alcoholic alizarin solution becomes yellow in the presence of fluorine ions Brown *zirconium p dimethyl aminoazobenzenearsinate,*

$$Me_2N\,C_6H_4N.NC_6H_4\,AsO_3H_2,$$

is said to be more sensitive (Feigl and Rajmann, Mikrochem. 1932, 12, 133). *Titanium sulphate* and *hydrogen peroxide,* fluorides bleach the yellow-orange colour of pertitanic acid. Test paper made from brazilwood extract is reddened by hydrogen fluoride.

Chlorine.—A greenish yellow gas, it is usually recognised by its odour, its ability to bleach litmus or to turn starch potassium iodide paper blue. A reagent made from aniline (3 c.c.), *o*-toluidine (1 c c) in acetic acid (300 c.c of 20% solution) gives a blue colour, passing to violet, with chlorine or its oxides in dilute acid solution. Damp cobalt nitrate test paper is coloured blue by chlorine; bromine and iodine give green colours, but in a mixture of the halogens the blue colour is developed first. The presence of chlorine in water is usually detected by adding a 0 1% solution of *o*-tolidine in 10% hydrochloric acid, when a yellow to red colour appears.

Chlorides.—*Silver nitrate,* white precipitate insoluble in nitric acid, soluble in ammonia, potassium cyanide, or sodium thiosulphate; the precipitate becomes violet on exposure to light. *Manganese dioxide* and *strong sulphuric acid,* evolution of chlorine. *Potassium dichromate* and *strong sulphuric acid,* brown red fumes (CrO_2Cl_2) dissolving in water to a yellow solution which after neutralisation with ammonia gives a yellow precipitate with soluble lead salts

Insoluble chlorides are difficult to detect by this method, but when digested with zinc and dilute sulphuric acid the solution contains chlorine ions.

Hypochlorites.—These are strong oxidising agents bleaching indigo or litmus, but having no action on potassium permanganate; their solutions are unstable and consequently give white silver chloride with silver nitrate. *Most acids* (including CO_2) liberate chlorine in the cold. *Metallic mercury,* yellowish-red deposit when shaken with test solution (Hg_2OCl_2). A solution of phenol (8 parts) and aniline (1 part) in water (200 parts) gives a blue colour with hypochlorites.

Chlorites.—Strong oxidising agents, especially in acid solution, bleaching indigo and litmus even in the presence of arsenious oxide (distinction from hypochlorites) They also bleach permanganate, forming brown hydrated manganese dioxide. *Dilute sulphuric acid,* development of yellow colour due to formation of ClO_2. Chlorides and hypochlorites accelerate this reaction while arsenious oxide retards. *Soluble lead* or *silver salts,* yellow or white precipitate. *Acidified ferrous sulphate,* transient violet colour. Chlorous acid gives with brucine, diphenylamine, etc., similar colours to those produced by nitric and chloric acids

Chlorates.—*Strong sulphuric acid,* yellow explosive chlorine dioxide is evolved on warming. *Indigo solution* is bleached with acidified solution only on warming, but in presence of sulphur dioxide, the reaction takes place in cold *Hydrogen peroxide* and *nitric acid,* chlorates are reduced to chlorides (distinction from bromates and iodates). *Potassium iodide* and *mineral acid,* iodine is liberated. If acetic acid is used no iodine separates even on long standing (distinction from iodates). All chlorates when ignited give chlorides, with brucine, diphenylamine, etc. chloric acid gives colours similar to those given by nitric acid

Perchlorates.—Unlike other oxygenated chlorine acids, perchloric acid is not reduced by hydrochloric acid or by a zinc copper couple; it is, however, reduced by titanous sulphate. Perchlorates give neither chlorine nor chlorine dioxide with hot sulphuric acid. *Potassium salts,* colourless crystalline precipitate from cold moderately strong solutions. *a Phenyl β diethylaminoethyl p nitrobenzoate,*

$$O_2N\,C_6H_4{\cdot}CO_2CHPh{\cdot}CH_2{\cdot}NEt_2,$$

in hydrochloric acid solution, light yellow precipitate (Cl^-, Br^-, ClO_3^-, IO_3^-, SO_4^{--}, CO_3^{--} do not interfere). *Strychnine sulphate,* colourless precipitate. Fusion with sodium carbonate converts perchlorates into chlorides.

Bromine.—Bromine, at ordinary temperatures, a brownish-red liquid evolving brown fumes with a suffocating odour, dissolves in carbon disulphide to a brown solution and gives a yellow colour with starch solution. Fluorescein (2% solution in 50% acetic acid) is converted by it into red eosin, while reduced fuchsin solution (2% solution reduced with excess of sulphur dioxide) is coloured violet (chlorine

and iodine do not interfere) (Hahn, Mikrochem. 1935, **17**, 222; López, Farm. moderna, 1935, **46**, 55). Bromine gives a colourless solution with ammonia.

Bromides.—*Silver nitrate*, pale yellow precipitate, insoluble in nitric acid, moderately soluble in ammonia, easily soluble in potassium cyanide or sodium thiosulphate. *Strong sulphuric acid*, liberation of hydrogen bromide and bromine on heating. *Strong sulphuric acid* and *manganese dioxide*, evolution of bromine only. *Strong sulphuric acid* and *potassium dichromate*, evolution of bromine only on heating. *Chlorine water* liberates bromine soluble in carbon tetrachloride or carbon disulphide to an orange-brown solution.

Bromates.—Alkaline and alkaline earth bromates give bromides and oxygen on heating; heavy metal bromates usually yield oxygen, bromine, and the oxide. *Strong sulphuric acid*, colourless solution gradually becoming brown with liberated bromine. *Dilute sulphuric acid*, colourless stable solution, but the addition of a little potassium bromide produces free bromine. *Silver nitrate*, white precipitate decomposed by hot hydrochloric acid with evolution of bromine. *Dilute oxalic acid* liberates carbon dioxide and free bromine. Methyl orange is rapidly decolorised by bromates in $4N$-hydrochloric acid (chlorates and iodates do not interfere).

Iodine.—Blue-black solid dissolving in carbon tetrachloride or disulphide to violet solutions, iodine is easily detected by the blue adsorption complex formed with cold starch solution. The element also gives a characteristic violet vapour on heating.

Iodides.—*Silver nitrate*, yellowish-white precipitate, insoluble in dilute nitric acid, sparingly soluble in ammonia, soluble in potassium cyanide or in concentrated KI or $NaCl$ or HCl solutions. *Strong sulphuric acid* and heat, iodine is evolved without the use of other oxidising agents. *Chlorine* or *bromine water*, liberation of iodine. *Sodium nitrite* and *dilute mineral* or *acetic acid*, iodides generate iodine but bromides do not give bromine except with large excess of nitrous acid. *Palladous chloride*, dark brown precipitate (PdI_2), insoluble in mineral acids, soluble in ammonia.

Iodates.—*Potassium iodide* and *dilute acid*, immediate precipitate of iodine. *Sulphurous acid*, liberation of iodine if reagent not in excess. *Silver nitrate*, white precipitate ($AgIO_3$), soluble in ammonia from which sulphur dioxide precipitates yellow silver iodide. *Barium chloride*, white precipitate, soluble in hot dilute nitric acid, or cold dilute hydrochloric acid; somewhat soluble in hot water. *Lead acetate*, white precipitate, $Pb(IO_3)_2$. *Mercuric chloride*, white precipitate.

The insolubility of the barium, mercuric, and lead iodates serves to distinguish iodic from bromic and chloric acids.

Periodates.—Most periodates have a low solubility but are easily dissolved in nitric acid. They are powerful oxidising agents, but iodine is only liberated with a certain excess of the reductant. *Silver nitrate*, yellowish-red or brown precipitates depending on the acidity of the solution; all become dark red if boiled with water. *Mercuric nitrate*, orange-red precipitate. *Mercurous nitrate*, yellow precipitate. *Tannin*, brown precipitate, soluble in ammonia; this solution becomes red on exposure to air.

Manganese. Manganous Salts.—*Ammonium sulphide*, pink precipitate (MnS), soluble in dilute acids. *Alkali* or *ammonium hydroxides*, white precipitate $\{Mn(OH)_2\}$, becoming brown in air; insoluble in excess. *Lead peroxide* and *nitric acid*, pink solution of permanganate. This oxidation may also be effected by potassium periodate, sodium bismuthate, or ammonium persulphate, though in the last case a trace of silver salt is necessary to catalyse the reaction. *Benzidine acetate* solution gives a blue colour with hydrated manganese dioxide.

Permanganates.—Soluble permanganates give red or purple solutions easily decolorised by reducing agents. *Strong sulphuric acid*, oxygen is evolved on heating and the colour destroyed. *Hydrochloric acid*, liberation of chlorine on warming. *Alkali hydroxides*, the red or purple colour becomes green (manganate):

$$4KMnO_4+4KOH=4K_2MnO_4+2H_2O+O_2$$

Manganates which readily decompose in acid solution,

$$3K_2MnO_4+2H_2SO_4$$
$$=2KMnO_4+MnO_2+2K_2SO_4+2H_2O,$$

give the foregoing reactions with hydrochloric and strong sulphuric acids.

Rhenium (as per-rhenates).—*Hydrogen sulphide* (in $4N$-acid solution), yellow colour followed by black precipitate (Re_2S_7). *Hydrazine hydrochloride* in alkaline solutions, black precipitate (ReO_2). *Nitron acetate*, colourless needles. *Potassium thiocyanate* and *stannous chloride*, yellow to red colour, soluble in ether. *Dimethylglyoxime* (saturated alcoholic solution) and stannous chloride (25% in concentrated HCl), yellow to red colour developing a green fluorescence on heating. Soluble potassium, silver and thallous salts give characteristic white crystalline precipitates from moderately strong solutions. Derivatives of quadrivalent rhenium are all coloured, easily oxidised to per-rhenates and deposit black rhenium dioxide with alkali.

Iron. Ferrous Salts.—*Hydrogen sulphide* or *ammonium sulphide*, black precipitate soluble in dilute acids. *Alkali hydroxides*, dirty green precipitate, incomplete in the presence of ammonium salts; readily oxidised to brown ferric hydroxide on exposure to air. *Potassium ferrocyanide*, pale-blue precipitate (white if pure). *Potassium ferricyanide*, dark blue precipitate. *Ammonium thiocyanate*, no colour if pure. 2:2′-*Dipyridyl* (1% solution in $0{\cdot}1N$-HCl), intense red colour; if manganese is present the solution should be at least $0{\cdot}2N$-with hydrochloric acid, while the presence of zinc calls for a considerable excess of the reagent. 2:2′:2″-*Tripyridyl*, intense purple coloration discernable with 1 part of $Fe^{\cdot\cdot}$ in two million).

Ferric Salts.—*Hydrogen sulphide* or *ammonium sulphide*, black precipitate ($FeS+S$) soluble in dilute acids. *Potassium ferrocyanide*, dark blue precipitate. *Potassium ferricyanide*, brown colour only. *Ammonium thiocyanate*,

intense red colour bleached by mercuric chloride. *Sodium phosphate*, yellowish-white precipitate, $FePO_4$, soluble in hydrochloric acid, insoluble in acetic acid. *Sodium acetate* in excess, dull red solution, deposition of a brown basic acetate on boiling.

Cobalt.—*Ammonium sulphide*, black precipitate insoluble in cold dilute hydrochloric acid. *Alkali hydroxides*, pale blue precipitate, slightly soluble in excess to a blue solution; ammonia produces, incompletely, the same precipitate, which is soluble in excess to a brown solution. *Potassium cyanide*, reddish brown precipitate soluble in excess forming $K_4Co(CN)_6$ which is oxidised on boiling in air to $K_3Co(CN)_6$; this solution gives no precipitate with soluble hypochlorites or hypobromites. *Potassium nitrite* in dilute acetic acid solution; yellow crystalline precipitate of $K_3[Co(NO_2)_6]$ *Ammonium thiocyanate* (concentrated solution), unstable blue colour, more stable in presence of acetone or amyl alcohol and ether. (Iron interferes and must be removed or its colour with the thiocyanate discharged with sodium fluoride.) If sodium mercuric thiocyanate, $Na_2Hg(SCN)_4$, be used then a blue precipitate is obtained. *α-Nitroso β naphthol* in acetic acid with neutral or slightly acid solutions, dark red precipitate (Cu, Fe, Ag, and Sn interfere). *Dithiooxamide* (rubeanic acid), in alcoholic solution added to ammoniacal test solution, yellow brown precipitate (Ni gives blue-violet solution).

Nickel.—*Ammonium sulphide*, black precipitate somewhat soluble in excess, insoluble in dilute hydrochloric acid. *Alkali hydroxides*, pale green precipitate, insoluble in excess, gives black $Ni(OH)_3$ with bromine water *Potassium cyanide*, greenish-yellow precipitate, soluble in excess forming $K_2Ni(CN)_4$, which is unaltered by boiling in air, hypochlorites or hypobromites give a black precipitate with this solution. *Dimethylglyoxime* with ammoniacal or acetic acid solution, scarlet precipitate. *Potassium xanthate* precipitates both nickel and cobalt from neutral solutions, but the former is soluble in ammonia and reprecipitated by ammonium sulphide. Nickel gives no precipitate with potassium nitrite and no colour with thiocyanate

Ruthenium.—Distillation with nitric and perchloric acids gives golden yellow crystals of RuO_4, soluble in sodium hydroxide to a reddish solution which is reduced by alcohol to black Ru_2O_3. *Hydrogen sulphide* with tervalent ruthenium; the solution becomes blue and a dark brown sulphide gradually forms; *ammonium sulphide* gives an immediate precipitate of the sulphide. *Sodium thiosulphate* with ammoniacal $Ru^{\cdots}$, purple red colour on warming. *Thiocarbamide* with hydrochloric acid solutions, blue colour; thiocarbanilide gives a blue green colour soluble in ether. *Potassium iodide*, black precipitate (RuI_3). *Strong aqueous ammonia* with ruthenium trichloride at 40° gives ruthenium red, $[Ru(OH)Cl(NH_3)_4]Cl,H_2O$, which dyes silk in reddish shades. Potassium ruthenichloride, K_2RuCl_6 (made by heating Ru with KCl in chlorine), gives a red to purple colour with potassium thiocyanate which changes to violet on warming. *2 2′-Dipyridyl* heated with ruthenium chloride and extracting with water, yellow colour.

Rhodium.—*The only platinum metal attacked* by strong sulphuric acid, is best converted into a soluble salt by heating with sodium chloride and chlorine; the resulting sodium rhodichloride, $Na_3[RhCl_6]$ crystallises from water in red prisms. Concentrated solutions give with ammonia a yellow precipitate of chloropentamminorhodium chloride, $[RhCl(NH_3)_5]Cl_2$, while warm potassium nitrite gives the sparingly soluble orange-yellow rhodinitrite,

$$K_3[Rh(NO_2)_6].$$

Other reactions of tervalent rhodium are given below. *Hydrogen sulphide*, slow formation of brown precipitate in the cold but more quickly on warming; insoluble in alkali sulphides, soluble in hot nitric acid. *Metallic zinc*, blue solution followed by deposition of the metal. *Benzidine*, rose yellow precipitate. *Potassium thiocyanate*, black precipitate. *Stannous chloride* (40% solution in conc. HCl), brown colour when heated, becoming red on cooling.

Palladium.—The most readily soluble of the platinum metals, it dissolves in aqua regia forming $PdCl_2$ and $PdCl_4$, and in nitric acid, when $Pd(NO_3)_2$ is obtained. Palladic salts are unstable except as double salts, of which the potassium and ammonium double chlorides are sparingly soluble and red in colour *Hydrogen sulphide* in acid solution, brown precipitate (PdS) insoluble in ammonium sulphide, soluble in boiling hydrochloric acid. *Alkali hydroxides*, brown precipitate soluble in excess of hot reagent *Potassium iodide*, black precipitate (PdI_2) soluble in excess, or in ammonia, to red solutions. *α-Nitroso β-naphthol* in acetic acid, red brown precipitate (distinction from other platinum metals) *Benzoylmethylglyoxime* in dilute acid solution, amorphous yellow precipitate; other platinum metals do not interfere. *Mercuric cyanide*, yellowish-white precipitate, $Pd(CN)_2$, soluble in ammonia or potassium cyanide.

Osmium.—Finely divided osmium is easily oxidised at ordinary temperatures; it readily burns in air above 425° forming osmium tetroxide, having a penetrating odour. This oxide (OsO_4) is also obtained by distilling osmium compounds with nitric acid when it distils and may be collected in sodium hydroxide solution, which becomes yellow due to the formation of sodium osmate (Na_2OsO_4). These osmates are unstable and lose osmium tetroxide on heating. *Hydrogen sulphide* in acid solution, dark brown precipitate (OsS_2) insoluble in ammonium sulphide. *Potassium thiocyanate* gives with acid solutions of the tetroxide a distinctive blue colour soluble in ether. *Thiocarbamide* and *dilute* HCl, intense red colour.

Osmium heated with potassium chloride in chlorine forms potassium osmichloride,

$$K_2[OsCl_6],$$

soluble in water to a red solution. Tannic acid reduces a hydrochloric acid solution of the double chloride, giving a blue solution of $OsCl_2$.

while potassium iodide develops a reddish-purple colour.

Iridium.—Only sparingly soluble in aqua regia even when finely divided, it is also unattacked by fusion with potassium pyrosulphate. Fusion with sodium peroxide leads to an oxide (IrO_3) which dissolves in aqua regia to a reddish-brown solution of $Na_2[IrCl_6]$. This iridichloride is more easily obtained by heating iridium with sodium chloride in a current of chlorine. This complex salt gives the following reactions: *Hydrogen sulphide*, brown precipitate after decolorisation of the solution. The sulphide (Ir_2S_3) is soluble in ammonium sulphide. *Alkalis*, colour changes from red to green and on boiling there is precipitated dark blue $Ir(OH)_4$, soluble in hydrochloric acid. Sodium hypochlorite or hypobromite gives the same precipitate. *Ammonium* or *potassium chloride*, reddish or dark brown precipitate giving an olive green solution with potassium nitrite which, boiled with excess of nitrite, becomes yellow, depositing yellowish-white $K_3Ir(NO_2)_6$ (separation from Pt). *Leuco base of malachite green* (1% solution in strong acetic acid), if a few drops of this reagent are added to the test solution then the presence of iridichloride restores the malachite green colour. The test is sensitive to one part iridium in six million. *Fuming sulphuric acid* and *ammonium nitrate* heated with iridium compounds give a blue coloration.

Platinum.—Platinum dissolves in aqua regia to form platinichloric acid, which gives the following reactions. *Hydrogen sulphide*, brown precipitate (PtS_2) soluble in ammonium sulphide, insoluble in acids except aqua regia. *Potassium* or *ammonium chloride*, yellow crystalline precipitate (M_2PtCl_6), slightly soluble in water, insoluble in alcohol. *Stannous chloride*, yellow to dark red colour depending on the concentration (distinction from Pd, Ir, Au). *Potassium iodide*, red to brown colour in dilute solutions. *Hydrazine hydrochloride* or *zinc* or *magnesium* with dilute hydrochloric acid, black precipitate (Pt).

The Inert Gases.—As these gases are almost devoid of chemical activity the ordinary methods of qualitative and quantitative analysis are not applicable to them and, therefore, they are determined by purely physical means. They are usually identified by their highly characteristic spectra, although the presence of Emanation (Radon, Niton) is more easily detected by means of its radioactive properties. In most cases it is necessary to concentrate the gases before applying spectrum analysis, since the sensitivity of this method is often considerably depressed by the presence of contaminating gases such as hydrogen, oxygen, nitrogen, hydrocarbons, etc. Partial separation is also desirable in order to detect small amounts of helium, krypton and xenon in mixtures of the inert gases. Tables of the most suitable lines for spectrum analysis may be found in the articles on the individual gases.

The purity of any sample of one of these rare gases is usually determined by measurements of density, dielectric cohesion, or the velocity of sound in the gas. G. T. M., G. R. D.

DROP REACTIONS ("SPOT" TESTS).

The methods described under this heading aim at the formation of a coloured spot on adsorbent paper, or on a white porcelain surface. In addition, it has become customary to include also many delicate tests which are more conveniently conducted in small test-tubes or capillaries. The tests, although qualitative, *are frequently extremely delicate. A feature of special interest is the wide adoption of organic* reagents used to detect inorganic ions. In applying these methods, their limitations, some of which are indicated below, should be remembered and control tests applied whenever possible. In carrying out "spot" tests it is important to use paper of suitable texture, since the drops should be adsorbed slowly without undue spreading. Many of the "spot" tests which have been proposed are merely adaptations of well-known standard reactions to this particular technique and therefore will not be included in the following selection of the essential practical details of those methods peculiarly suited to microchemical application.

METALS.

Aluminium.—A strip of adsorbent paper is soaked in an alcoholic solution of alizarin and dried. A drop of the solution to be tested is spotted on the paper, which is then exposed to ammonia vapour and dried; the violet colour of the ammonium alizarinate is discharged, and the presence of aluminium is revealed by a red spot. The test will detect 0·3μg. Al (Feigl and Stern, Z. anal. Chem. 1921, **60**, 9). Interference of Fe, Cr, U, Th, Ti, and Mn may be obviated by using paper previously treated with potassium ferrocyanide, whereby insoluble ferrocyanides are formed and the Al solution spreads beyond as a damp ring; an alcoholic solution of alizarin is now added to the spot, and the test completed as before.

Antimony.—Two drops of the solution are added to an equal volume of strong hydrochloric acid, and a small crystal of sodium nitrite is dissolved in the mixture; one drop of this solution is added to 0·2 c.c. of a 0·01% aqueous solution of rhodamine-B in a depression of a spotting tile. The presence of quinquivalent antimony is indicated by a colour change from red to violet and the formation of a precipitate. Sn and small amounts of Fe do not interfere, but Bi, Hg, Au, Th, Mo, and W must be absent. The test will detect 1μg. Sb in the presence of 12,500 times as much Sn (Eegriwe, Z. anal. Chem. 1927, **70**, 400).

Barium.—The solution to be tested is spotted on adsorbent paper, and a drop of a 0·1% aqueous solution of the sodium salt of rhodizonic acid (dihydroxydiquinoyl) added; the presence of Ba is indicated by the appearance of a reddish-brown spot of barium rhodizonate which changes to brilliant red on the addition of dilute hydrochloric acid. Ca does not react, while the colour produced by Sr is destroyed by the hydrochloric acid. The test detects 0·25μg. Ba. In the absence of Ba the reagent serves as a test for Sr, the hydrochloric acid being omitted (Feigl, Mikrochem. 1924, **2**, 188).

Beryllium.—The reagent consists of a freshly prepared 0·25% solution of quinalizarin (1.2.5.8-tetrahydroxyanthraquinone) in 0·25*N*-**NaOH**, a drop of which is placed on adsorbent paper previously moistened with a drop of the solution to be tested. A bright blue spot is indicative of **Be**. If **Al** is present the solution under test should contain sufficient sodium hydroxide to prevent the precipitation of aluminium hydroxide. **Pb**, **Zn**, and **Sn** are without influence, while the effect of **Cu**, **Ni**, and **Co** can be eliminated by using cyanide. **Zr**, **Ce**, **Th**, and many rare earth metals behave similarly to **Be**. **Mg** also produces a bright blue lake, but the colour is destroyed by very dilute bromine water, while that due to **Be** is relatively stable. The test will detect 0·14μg. **Be** (Fischer, Wiss. Veröff. Siemens Konz. 1928, 5, 99; Z. anal. Chem. 1928, 73, 54).

Bismuth.—Adsorbent paper is spotted with a reagent containing 1% of cinchonine and 2% of potassium iodide in dilute nitric acid and then with the solution; the presence of bismuth is indicated by an orange red spot. If **Hg** is also present, an orange circle forms around a white central zone, while if **Pb** and **Cu** are also present the test is still applicable, since the two last metals produce yellow and brown rings outside the orange area due to **Bi**. The test detects 0·14μg. **Bi** (alone) or 10μg in presence of the other three metals mentioned (Feigl and Neuber, Z. anal Chem. 1923, 62, 273).

Cadmium.—A drop of the solution under test, neutral or faintly acid with acetic acid, is spotted on adsorbent paper impregnated with an alcoholic solution of diphenylcarbazide (Feigl and Neuber, Z. anal. Chem. 1923, 62, 369). A violet spot on exposure to ammonia vapour indicates **Cd**, the test is sensitive to 4μg. of **Cd**. Magnesium also gives the reaction.

The addition of a saturated aqueous solution of 3-nitro-4-hydroxyphenylarsonic acid to a solution of a cadmium salt in 10% acetic acid buffered with sodium acetate produces a yellow crystalline precipitate (Pavelka and Kolmer, Mikrochem. 1930, 8, 277). This test, stated to be specific for **Cd**, detects 35μg in one drop of solution.

Calcium.—The liquid under test (neutral or acidified with acetic acid) is added to a drop of a saturated aqueous solution of picrolonic acid contained in the depression of a *warm* spotting tile. In the presence of **Ca**, characteristic rectangular crystals are produced, the test being sensitive to 0·01μg. (Kisser, Mikrochem. 1923, 1, 25).

Chromium.—The solution under test, acidified with acetic or sulphuric acid, is added to a drop of a 0·2% solution of diphenylcarbazide in a mixture of 1 part of glacial acetic acid and 9 parts of ethyl alcohol. The presence of chromate is indicated by the production of a violet colour. The test will detect 0·25μg. **Cr.** Chromium salts should first be oxidised with bromine water, excess bromine being removed by phenol (Stover, J. Amer. Chem. Soc. 1928, 50, 2363). Other metals, including **Ag**, **Hg**, **Cu**, **Pb**, **Ni**, and **Co**, give colours.

Cobalt.—A drop of the solution, neutral or only slightly acid, is placed on adsorbent paper, and a 0·05% aqueous solution of α-nitroso-β-naphthol rendered slightly alkaline with sodium hydroxide is added. A brown spot is produced in the presence of **Co**. The test will detect 0·005μg. **Co** (Feigl and Stern, Z. anal. Chem. 1921, 60, 31). Cuprous salts do not interfere, but cupric compounds, if present, must be reduced. The interference of **Fe** and **U** may be obviated by first adding ammonium phosphate.

Copper.—The test liquid is spotted on to adsorbent paper impregnated with a 2% alcoholic solution of α-benzoin oxime and dried. The presence of **Cu** is revealed by the formation of a green coloration on exposure to ammonia vapour. The test will detect 0·1μg. **Cu**. The interference of other metals may be obviated by treating the test liquid with ammoniacal tartrate (Feigl, Ber. 1923, 56, [B], 2083; Mikrochem. 1923, 1, 76).

In the absence of **Ag**, **Hg**, and the noble metals, a 0·03% solution of *p*-dimethylaminobenzalrhodanine serves as a delicate test for cuprous ions, with which it forms a violet coloration or precipitate in neutral or acid media. No colour is yielded by cupric ions (Funakoshi, Mem. Coll. Sci. Kyoto, 1929, 12, 155).

Lead.—A drop of the solution is placed on adsorbent paper, followed by a drop each of 1% aqueous pyridine solution and an aqueous solution containing 0·1% of gallocyanine and 0·1% of sodium bicarbonate. Excess of the reagent is removed by washing with pyridine solution. A deep violet spot is produced by 6μg. **Pb**. In the presence of **Ag**, **Cu**, **Bi**, and **Cd** the solution should be spotted on paper and foreign metals removed by washing with dilute sulphuric acid followed by alcohol. The paper is dried and the test applied (Pavelka, Mikrochem. 1929, 7, 303).

Magnesium.—The liquid is rendered acid with hydrochloric acid and transferred to the depression of a porcelain tile, and a drop of a 0·5% solution of *p*-nitrobenzeneazoresorcinol in 0·25*N* **NaOH** is added. On rendering alkaline with sodium hydroxide, a sky-blue colour indicates the presence of **Mg**; **Ca** does not interfere, but **Be**, **Al**, **Zn**, **Cd**, **La**, **Co**, and **Ni** mask the reaction. The test will detect 0·05μg. **Mg**, but for delicate work it is better to use a more dilute reagent solution (Suitsu and Okuma, J. Soc. Chem. Ind. Japan, 1926, 29, 132; Ruigh, J. Amer. Chem. Soc. 1929, 51, 1456; Engel, *ibid.* 1930, 52, 1812). Another reagent, used similarly, is *p*-nitrobenzeneazo-α-naphthol.

Mercury.—Adsorbent paper is impregnated with a freshly prepared saturated alcoholic solution of diphenylcarbazone and then treated with a drop of the solution under test; the presence of mercury is shown by a violet-blue spot. **Pb**, **Cu**, **Sn**, **Cd**, **Ni**, and **Co** interfere, and **Ag**, **Sb**, **As**, **Fe**, **Cr**, **Al**, **Mn**, and **Zn** slightly impair the value of the test. The reaction of the solution influences the sensitivity which is at its maximum at p_H 7–8, when it will detect 0·1μg. **Hg**. Chlorides, bromides, iodides, and cyanides diminish the sensitivity (Feigl and Neuber, Z. anal. Chem. 1923, 62, 370; Cucuel, Mikrochem. 1933, 13, 321 *et seq.*).

Nickel.—The liquid is rendered alkaline with dilute ammonia and a drop of a 10% alcoholic solution of α-furildioxime added; the presence of Ni is indicated by a red coloration or precipitate. The test will detect 0·02μg. Ni; it is not disturbed by Ag, Cu, or by ferric iron, Cr or Al in the presence of ammoniacal tartrate solution. If Zn is present, ammonium chloride should first be added. Cobaltous ions depress the sensitivity and should be oxidised to cobaltic with hydrogen peroxide. Ferrous iron interferes; it should be oxidised and alkaline tartrate added before applying the test (Soule, J. Amer. Chem. Soc. 1925, **47**, 981; Harwood and Theobald, Analyst, 1933, **58**, 673).

Potassium.—A reagent solution is prepared by dissolving 0·2 g. of hexanitrodiphenylamine in 20 c.c. of boiling 0·1*N*-Na_2CO_3, cooling and filtering. A drop of the neutral solution under test is placed on adsorbent paper and the reagent solution immediately added; an orange-red fleck is produced which, in the presence of potassium, remains unchanged on the addition of two drops of 0·1*N*-HCl, but otherwise fades to a sulphur-yellow colour. The test will detect 30μg. K and is applicable in the presence of 80 times as much Na and 130 times as much Li; Mg, Sr, Ca, and Ba do not interfere, but ammonium salts should be removed. Rb and Cs react similarly to K (Poluektov, Mikrochem. 1933–34, **14**, 265).

Silver.—The liquid is spotted on to adsorbent paper and a drop of *N*-HNO_3 added, followed by a trace of a 0·03% solution of *p*-dimethylaminobenzalrhodanine in acetone. In the presence of Ag a reddish-brown spot is produced, the test being sensitive to 0·01μg. A similar colour is also given by Hg, Au, Pt, Pd, and cuprous ions. The final addition of a drop of 0·1*N*-HCl inhibits the reaction due to relatively large amounts of Hg without influencing the sensitivity for Ag. The interference of Au, Pt, and Pd may be largely obviated by first adding a little potassium cyanide.

Strontium.—*See* under Barium.

Tin.—Adsorbent paper is impregnated with a saturated aqueous solution of cacotheline and the liquid under test is treated with hydrochloric acid and zinc and then spotted on the prepared paper. The presence of Sn is indicated by a violet spot surrounded by a less coloured zone on the yellow paper. The test is sensitive to 2μg. Sn. It cannot be applied in the presence of Ag, Cr, Co, $Fe^{\cdots}$, Hg, Co, Ni, Mo, or V; antimonious compounds cause a slight interference, and titanous chloride reacts in the same way as stannous salts. Hyposulphites also react with the reagent, while sulphites, bisulphites, and selenites disturb the test (Leuchs and Leuchs, Ber. 1910, **43**, 1042; Gutzeit, Helv. Chim. Acta, 1929, **12**, 720; Newell, Ficklen, and Maxfield, Ind. Eng. Chem. [Anal.] 1935, **7**, 26).

Titanium.—The liquid to be examined is placed on a tile or on adsorbent paper, and one drop of a 5% aqueous solution of sodium 1:8 - dihydroxynaphthalene - 3:6 - disulphonate (chromotropic acid) added. The formation of a reddish-brown colour indicates Ti, the test being capable of detecting 5μg. Hg, Ag, U, and $Fe^{\cdots}$ also give colorations, but their interference may be obviated by warming the liquid with a hydrochloric acid solution of stannous chloride, centrifuging, and adding the reagent to the supernatant liquid (Hofmann, Diss., Munich, 1902; Tananaev and Patschenko, Z. anorg. Chem. 1926, **150**, 163).

Zinc.—A convenient quantity of the liquid is added to 1 c.c. of a 10% alcoholic solution of resorcinol containing one drop of ammonia solution and allowed to stand for some hours, a control being prepared simultaneously. In presence of Zn the solution changes first to golden-yellow, then to green, and finally to deep blue. The test is sensitive to 2μg. Zn, but its application is rather limited (Sensi and Testori, Annali Chim. Appl. 1929, **19**, 383).

Zirconium.—A drop of the acidified liquid is spotted on adsorbent paper impregnated with a solution of 0·1 g. of *p*-dimethylaminobenzeneazophenylarsonic acid in 5 c.c. of concentrated hydrochloric acid and 100 c.c. of alcohol. The presence of Zr is revealed by a brown fleck. If excess of reagent is removed by immersing the paper in 2*N*-HCl warmed to 60°, it is possible to detect 1μg. Zr; tantalum reacts similarly, and sulphates, phosphates, and fluorides interfere. Mo, W, Ti, and Sn also interfere, but a technique is available for use in presence of these metals (Feigl, Krumholz, and Rajmann. Mikrochem. 1931, **9**, 395).

Non-metals.

Bromine.—Adsorbent paper, which has been impregnated with a dilute alcoholic solution of fluorescein and dried, is placed on the mouth of a micro-test tube containing the liquid to be tested mixed with acetic acid and lead dioxide. The tube is heated over a flame, and the presence of liberated bromine is revealed by a red spot on the paper due to the formation of eosin. The test will detect 2μg. Br. Iodine also forms a red spot due to erythrosin (Ganassini, Chem. Zentr. 1904, **1**, 1172).

Sulphur.—The substance to be examined, contained in a micro-test tube, is mixed with a trace of benzylimidodi-(*p*-methoxyphenyl)-methane, and the tube placed for 5 minutes in an oil bath at 210°C. After cooling, two drops of benzene are added, and in the presence of elemental sulphur the solvent will be coloured blue. If a crystal of mercuric chloride be added to the separated liquid, the blue slowly fades and the crystal becomes red or orange. The test will detect 100μg. of elemental sulphur, and does not react to sulphur in combination (Schönberg and Urban, Ber. 1934, **67**, [B], 1999).

Acid Radicals.

Borates.—The liquid under test is evaporated to dryness in a porcelain crucible and a drop of a 0·005% solution of chromotrope 2B (sodium salt of *p*-nitrobenzeneazochromotropic acid) in concentrated sulphuric acid added to the warm residue. A colour change from blue-violet to greenish-blue indicates boric acid. The test will detect 5μg. H_3BO_3. The interference of oxidising substances may be obviated by adding a little hydrazine sulphate before

evaporating the test liquid to dryness (Komarovsky and Poluektov, Mikrochem. 1933–34, 14, 317).

Cyanides.—*Adsorbent paper is moistened* with a mixture of equal parts of a 0 286% aqueous solution of normal copper acetate and benzidine acetate (475 c.c. of saturated solution diluted to 1 litre) and tied over the mouth of a *small test tube containing* the liquid under test mixed with dilute sulphuric acid. The presence of cyanides is indicated by the production of a blue colour, the test being sensitive to 0 25μg. CN' (Moir, Chem News, 1910, 102, 17; Sievert and Hermsdorff, Z. angew Chem. 1921, 34, 3).

Fluorides.—An excess of an alcoholic solution of alizarin is added to a 0 05% solution of ZrO_2 in dilute hydrochloric acid, and this solution used to impregnate adsorbent paper, which, after drying, is moistened first with 50% acetic acid and then with a drop of the neutralised test liquid. The presence of fluorides is indicated by a yellow stain on the reddish violet paper which is rendered more pronounced by exposing it to steam. Sulphates, oxalates, and phosphates interfere. The test will detect 8μg F' (de Boer, Chem. Weekblad, 1924, 21, 404, Pavelka, Mikrochem. 1928, 6, 149).

Nitrates.—A reagent is prepared by dissolving 0 085 g of diphenylbenzidine in a mixture of 50 c.c. of water and 450 c c of sulphuric acid (nitrate-free). A capillary tube is half filled with the reagent, and then the liquid to be tested is drawn into the same tube. The presence of nitrates is indicated by a blue colour developing within 15 minutes, 0·1 part of NO_3' per million of solution being detectable (Hamence, Analyst, 1935, 60, 532) The method is applied to the detection of added water in milk, the serum being prepared by adding 6 drops of a solution containing 20% of mercuric chloride and 5% of ammonium chloride in 20% of concentrated hydrochloric acid to 5 c.c of milk, shaking, and filtering off the serum, which is then tested for nitrate, which is present in water and totally absent from milk (Lerrigo, Analyst, 1930, 55, 435; Monier-Williams, *ibid.* 1931, 56, 397).

Phosphates.—The liquid under test is placed on adsorbent paper, followed by a drop of nitromolybdate solution containing 15% of tartaric acid; after warming over a flame, a 0 5% solution of benzidine in 10% acetic acid is added, and the paper exposed to ammonia vapour. A blue colour indicates phosphates, the test being sensitive to 1 5μg. P_2O_5 Arsenates and silicates do not react (Feigl, Z. anal. Chem. 1929, 77, 299).

Silicates.—A drop of the solution under test is mixed with two drops of nitro-molybdate solution, the mixture centrifuged and the supernatant liquid gently warmed, cooled, then treated with two drops of 1% oxalic acid, a drop of 0 5% solution of benzidine in 10% acetic acid and a little saturated sodium acetate solution. The mixture is spotted on *adsorbent paper and this is exposed to ammonia* vapour, the presence of a silicate being indicated by a blue colour. The test will detect 6μg. SiO_2 in the presence of 250 times as much P_2O_5 (Feigl and Krumholz, Mikrochem., Pregl-*Festschrift*, 1929, 82).

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N. L. A.

QUANTITATIVE ANALYSIS.

Gravimetric Methods.

Most of the chemical elements are weighed in the form of one or other of their compounds although a few are estimated in the elementary condition. Compounds used for such determinations should be stable, non-hygroscopic, and of a perfectly definite composition and insoluble in the solution in which they are formed and in excess of the reagent; they must be easily freed from impurities and capable of being brought into condition for weighing without tedious and complicated operations Furthermore, they should contain only a small proportion of the constituent to be estimated, since the effect of experimental errors is thus minimised For this reason increasing use is made of organic reagents with large molecules or of complex inorganic compounds As an example may be cited the estimation of sodium as sodium zinc uranyl acetate in which the percentage of sodium is only 1·495 and, therefore, a little sodium gives a large weight of precipitate.

It is, to day, impossible to generalise the methods of estimation, as the number of procedures in use is far too great and too diverse A few of the more typical operations and separations are, however, briefly described.

Precipitation as Sulphides.

(*a*) *With Hydrogen Sulphide*—Estimations as sulphides are avoided wherever possible, but separations as such are of considerable importance and, moreover, can be carried out under varied conditions. Thus, variation of the hydrogen ion concentration leads to a separation of arsenic from antimony, bismuth, lead, zinc, etc., or of zinc from nickel, nickel from manganese. Certain metals can also be converted into complex ions unaffected by this reagent leading to separations of cadmium from copper in cyanide solution, antimony from tin in oxalic acid solutions, arsenic from germanium in hydrofluoric acid. For complete separations careful adjustment of the p_H value of the solution is often necessary, as an insufficient acidity will often lead to the co-precipitation of thallium, indium, gallium, vanadium, tungsten, or zinc with the copper or arsenic groups.

(*b*) *With Alkali or Ammonium Sulphide.*—Ammonium sulphide is generally used, but sometimes it is preferable to use sodium sulphide or hydrosulphide or sodium thiosulphate. Where the reagent is used to precipitate iron, zinc, *manganese, etc, it is usual to add ammonium*

chloride to prevent any precipitation of magnesium. If it is desired to prevent the precipitation of metals like aluminium which form hydroxides then tartaric acid must be present. Ammonium or alkali sulphides are also used to precipitate the copper in the presence of the arsenic group.

Precipitation as Hydroxides.

(*a*) *With Ammonia.*—Ammonia, especially in the presence of ammonium salts, is chiefly used for separating the members of the third analytical group from those of the later groups. For accurate results it is necessary to carry out the precipitations with due regard to the proper conditions for each case and, generally speaking, any appreciable excess of ammonia should be avoided. Organic compounds, borates, arsenates, phosphates, and vanadates interfere with this separation and must either be removed or other methods adopted. Hexamethylenetetramine may replace ammonia, while it is sometimes advantageous to use weaker bases such as aniline or phenylhydrazine.

(*b*) *With Suspensions of Carbonates.*—Satisfactory separations are often obtained by shaking the solution with freshly precipitated barium or calcium carbonate. Cadmium carbonate has also been used for removing ferrous iron from chromium and vanadium.

(*c*) *By the Basic-Acetate Method.*—This method, less used than formerly, is carried out by neutralising the solution as far as possible without producing a permanent turbidity and adding sodium acetate to the hot solution and boiling for 3 minutes. The precipitate is filtered as soon as it has settled and should not be allowed to cool or some of it may redissolve.

In certain cases a better precipitate is obtained by hydrolysing with ammonium nitrite and methyl alcohol (*see* BERYLLIUM).

Precipitation with Organic Reagents.

(*a*) *Cupferron* (ammonium *N*-nitrosophenylhydroxylamine).—This reagent, generally used as a 6% aqueous solution, provides quantitative separations of iron, vanadium, zirconium, titanium, tin, niobium, tantalum, and quadrivalent uranium from aluminium, beryllium, phosphorus, manganese, nickel, and hexavalent uranium. Precipitations are generally carried out in cold acid solutions. The precipitates are unsuitable for weighing as such but are easily ignited to the oxides. Excepting uranium, the metals should be in their higher valencies, while the solution usually contains about 10% (by volume) of sulphuric acid, although with uranous salts a lower acidity is necessary.

(*b*) 8-*Hydroxyquinoline* (Oxine).—Oxine gives precipitates with a large number of metals and is a useful quantitative reagent. By suitably choosing the experimental conditions many valuable separations are also possible. Thus in ammoniacal solution it provides a clean separation of magnesium from the alkali metals. In acetic acid–acetate solutions it removes aluminium from magnesium and beryllium, while in ammoniacal–hydrogen peroxide media the previously mentioned metals may be separated from molybdenum, vanadium, titanium, niobium, and tantalum. Ammoniacal ammonium carbonate prevents the precipitation of uranium. The reagent is used in alcoholic or acetic acid solution.

The oxine precipitates may often be weighed as such, but it is generally preferable to dissolve them in hydrochloric acid and titrate the solution with bromate–bromide (*see* VOLUMETRIC ANALYSIS, p. 650).

(*c*) *Quinaldinic Acid.*—Like oxine, quinaldinic acid gives insoluble salts (or basic salts) with many metals, but the right choice of conditions enables separations to be made. Thus copper may be separated from Cd, Pb, Hg, Mn, Ni, Co, PO_4''', AsO_4''', by precipitation in hot dilute sulphuric acid solution. Zinc in dilute acetic acid may be separated from manganese and the alkaline earths, while the presence of alkaline tartrate also prevents precipitation of $Fe^{\cdots}$, Al, Be, Ti, and U (Rây and others, Z. anal. Chem. 1933, **95**, 400; 1935, **100**, 324; Mikrochem. 1935, **17**, 11).

Gravimetric Determination of the Elements.

Lithium.—When present alone lithium is best estimated as sulphate, though precipitation as phosphate or fluoride may also be used. The last two methods give fair separations from other alkali metals, but where these are present the lithium is best removed by taking advantage of the solubility of certain of its salts in organic media. Thus from a mixture of the anhydrous chlorides the lithium salt may be separated by means of dioxan, acetone, amyl alcohol, *iso*butyl alcohol, or pyridine. In each case the solvent must be perfectly dry, although when acetone is used one drop of concentrated hydrochloric acid is added to prevent the formation of lithia.

These extractions are best carried out by the procedure advocated by Sinka for dioxan (Z. anal. Chem. 1930, **80**, 430). The weighed mixture of alkali chlorides is placed in a sintered glass crucible which is suspended just above the surface of the solvent in a suitable flask fitted with a reflux condenser, and the liquid is gently boiled for some hours. The condensate drips into the crucible and effectively extracts the lithium chloride, which is determined by the loss in weight of the crucible and, if necessary, by estimation of the dissolved salt either as sulphate or volumetrically with silver nitrate (Brown and Reedy, Ind. Eng. Chem. [Anal.], 1930, **2**, 304; Gooch, Chem. News, 1887, **55**, 78; Winkler, Z. anal. Chem. 1913, **52**, 628; Kahlenberg and Krauskopf, J. Amer. Chem. Soc. 1908, **30**, 1104; Moser and Schutt, Monatsh. 1929, **51**, 23).

Yagoda recommends the extraction of lithium bromide with *iso*amyl alcohol, in which case magnesium, strontium, calcium, and lithium alone of the alkali and alkaline earth bromides dissolve. Conversion into the nitrates and ignition removes magnesium as oxide, while strontium is separated by virtue of the insolubility of its nitrate in *iso*amyl alcohol. Calcium is then precipitated as oxalate and lithium as the stearate (J. Amer. Chem. Soc. 1930, **52**, 3068; 1932, **54**, 984).

Lithium may also be separated from the other alkali metals by extracting the perchlorates with ethyl acetate and *n* butyl alcohol (1 : 1) (Smith and Ross, J. Amer. Chem. Soc. 1925, **47**, 1020), but Moser and Schutt (*l c.*) state that this method gives low results.

A solution of sodium arsenate with excess of ammonia and enough alcohol to produce a faint turbidity gives a pink precipitate with lithium; other alkali metals do not interfere, while magnesium may be previously removed with sodium arsenite (Gaspar y Arnal, Ann. Chim. Analyt. 1933, (ii), **15**, 193). Magnesium is, however, best removed with 8-hydroxyquinoline (Moser and Schutt, *l.c.*).

Sodium.—Sodium may be estimated as sulphate or, if potassium is present, as chloride; in the latter case the potassium is determined as platinichloride and the sodium found by difference.

A useful method for sodium and one which accomplishes a fair separation from other alkali metals is by means of zinc (or magnesium) uranyl acetate, whereby a crystalline precipitate of the triple salt,

$$NaM(UO_2)_3(C_2H_3O_2)_9,6H_2O,$$

is obtained (M=Zn or Mg). This precipitate, although soluble in water, is insoluble in excess of the reagent or in alcohol or ether The zinc uranyl acetate is made by dissolving 200 g. of zinc acetate and 70 g of uranyl acetate in 60 ml of glacial acetic acid and 940 ml of water, the solution being filtered after standing for some hours at room temperature. The neutral sodium solution containing not more than 6 mg. of the metal per ml. is treated with ten times its volume of reagent and the mixture allowed to stand for one hour with occasional stirring The precipitate is filtered through a sintered glass crucible, washed five times with 2 ml. portions of the reagent, then with alcohol saturated with the triple acetate and finally with ether. It is weighed after drying for 15 minutes at 40°. 1 g. of the zinc triple salt=14 95 mg Na.

Kahane (Bull. Soc chim. 1933, [iv], **53**, 555) suggests the following as the best magnesium reagent: uranyl acetate 25 g, magnesium acetate 150 g, acetic acid 780 g., and enough water to make up to one litre. Using this it is only necessary to take a volume equal to that of the solution while it gives no precipitate with less than a 10% solution of potassium chloride or a 1% solution of lithium chloride. Phosphates and oxalates interfere in these estimations. (Zn *salt*.—Kolthoff, Z. anal. Chem. 1927, **70**, 397; Barber and Kolthoff, J. Amer. Chem. Soc. 1928, **50**, 1625; 1929, **51**, 3233; Mg *salt*: Kolthoff, Pharm Weekblad, 1923, **60**, 1251; Caley and others, J. Amer. Chem. Soc. 1929, **51**, 1664; 1930, **52**, 41, 1349; 1932, **54**, 1344; Ind. Eng. Chem. [Anal.] 1934, **6**, 202; Kahane, Bull. Soc. chim. 1930, (iv), **47**, 382; Ni *salt*: Feldstein and Ward, Analyst, 1931, **56**, 245.)

Various volumetric methods of estimating the triple acetate precipitates have also been recommended.

Potassium.—This third member of the alkali group is usually estimated as sulphate, platinichloride, perchlorate, or less successfully as cobaltinitrite.

(*a*) *Platinichloride Method.*—When sodium (or lithium) is present the determination is made as follows. A weighed mixture of the chlorides is dissolved in a little water and sufficient platinichloric acid added to convert them completely into the complex salts. The mixture is then evaporated in a porcelain basin nearly to dryness and the residue extracted with alcohol (80-85%), which is decanted through a small filter paper; the extraction is continued until the residue is golden-yellow and shows no orange red colour. The residue and filter paper are dried separately and any precipitate on the paper is dissolved in a little warm water, the solution being caught in a weighed platinum crucible or dish, after which it is evaporated to dryness. The platinichloride in the dish is now added with the aid of a little water, the solution again evaporated, and the salt is finally dried at 130° for one hour.

When potassium alone is present it is usual to add a few drops of hydrochloric acid before precipitation, but otherwise the procedure may be carried out as above.

It has been usually stated that the potassium must be in the form of chloride and that metals of the other analytical groups must be absent, but O'Leary and Papish (Ind Eng Chem [Anal], 1934, **6**, 107) state that potassium, rubidium, or cæsium may be quantitatively precipitated in alcohol without contamination even in the presence of fair amounts of sodium, aluminium, iron, or manganese provided all the metals are present as nitrates.

Instead of weighing the platinichloride, it may be dissolved in water and reduced with magnesium ribbon and hydrochloric acid to platinum, which is weighed About 0 5 g of magnesium is required for every 0 2 g of potassium present and before filtration the mixture is boiled with a few ml. of acid to dissolve any basic magnesium salts (Hicks, Ind. Eng. Chem 1913, **5**, 650; Wells, Bailey, and Fairchild, *ibid.* 1924, **16**, 935).

(*b*) *As Perchlorate*, $KClO_4$.—This method also serves as a separation from sodium and lithium

The mixed chlorides are converted into perchlorates by evaporating to dryness twice with a few ml. of 60% perchloric acid at a temperature not exceeding 350°. The residue is extracted with absolute alcohol containing 0 2% perchloric acid and the extract decanted through a sintered glass or Gooch crucible. The residual potassium perchlorate may now either be transferred to the crucible with the aid of absolute alcohol saturated with potassium perchlorate or, for greater accuracy, it may be dissolved in water, evaporated to dryness with a little perchloric acid, and the extraction repeated before finally transferring to the crucible. The precipitate is dried at 130° (Baxter and Kobayashi, J. Amer. Chem. Soc. 1917, **39**, 249; Baxter and Ruppert *ibid.* 1920, **42**, 2046).

A mixture of butyl alcohol and ethyl acetate may be used instead of alcohol and in some ways is to be preferred (Willard and Smith, J. Amer. Chem. Soc. 1922, **44**, 2816; 1923, **45**, 293; Smith and Ross, *ibid.* 1925, **47**, 774, 1020).

Neither the platinichloride nor perchlorate method is entirely satisfactory when the percentage of sodium present is considerable, but Smith and Gring (J. Amer. Chem. Soc. 1933, **55**, 3957) claim that it is possible to estimate 0·15% of KCl in $NaCl$ by a combination of these methods. A solution of the perchlorates, containing not more than the equivalent of 1·6 g. of sodium chloride per 100 ml. in 95% aqueous ethyl alcohol is treated with platinichloric acid (0·2 g. per 100 ml. of solution) in the same medium. After digestion, the mixture is kept at 0° for one hour, filtered, washed once with 95% alcohol and then with absolute alcohol. The precipitate is then determined as either K_2PtCl_6 or Pt.

Rubidium and Cæsium.—The three alkali metals potassium, rubidium and cæsium so closely resemble each other that the task of obtaining even qualitative separations is not easy, while entirely accurate quantitative determinations of them have not yet been made.

Qualitative separations of potassium may be effected by:

(*a*) Fractional precipitation with platinichloric acid and strong hydrochloric acid (Robinson, Ind. Eng. Chem. 1918, **10**, 50).

(*b*) Precipitation of cæsium and rubidium as stannichloride, a method commonly used in qualitative analysis but which under quantitative conditions causes co-precipitation of potassium (Moser and Ritschel, Z. anal. Chem. 1927, **70**, 184; Burkser, Milgevskaja, and Feldman, Z. anal. Chem. 1930, **80**, 264).

(*c*) Sodium silicomolybdate has also been used technically to separate rubidium and cæsium from potassium (Jander and Busch, Z. anorg. Chem. 1930, **187**, 165; **194**, 38; Moser and Ritschel, Monatsh. 1925, **46**, 9).

The separation of cæsium from rubidium or potassium may be quantitatively accomplished with silicotungstic acid in 6*N*-hydrochloric acid (O'Leary and Papish, Ind. Eng. Chem. [Anal.] 1934, **6**, 107). The double compound with bismuth iodide, $Cs_3Bi_2I_9$, has also been recommended by Tananaev and Harmasch (Z. anal. Chem. 1932, **89**, 256), but Feldmann (*ibid.* 1935, **102**, 102) states that the method does not give accurate results. Various complexes with antimony chloride, especially the one with ferric chloride, have also been used (Strecker and Diaz, Z. anal. Chem. 1925, **67**, 321).

Potassium and rubidium may be qualitatively separated from cæsium by means of their sparingly soluble picrates, acid tartrates, or 6-chloro-5-nitrotoluene-3-sulphonates.

O'Leary and Papish (*l.c.*) have recently described a scheme for the quantitative separation and estimation of the three alkali metals which appears to be reasonably accurate. Use is made of luteo-phosphomolybdic acid (9-phosphomolybdic acid) which when added to a solution of the mixed chlorides in boiling nitric acid (3·5*N*) precipitates the rubidium and cæsium only, provided that the amount of potassium chloride does not exceed 1 g. per 100 ml. of solution. The potassium in the filtrate may be estimated in the usual way.

The phosphomolybdate precipitate is then dissolved in dilute alkali, the solution saturated with hydrogen sulphide and made just acid with nitric acid, when the molybdenum is precipitated as sulphide and filtered off. The cæsium in the filtrate is then precipitated as silicotungstate in 6*N*-HCl, though it is more satisfactory first to concentrate the two alkali metals as their platinichlorides and then to effect the separation. The cæsium is not weighed as silicotungstate but is converted into the platinichloride. For this purpose the precipitate is dissolved in sodium hydroxide, made faintly acid with nitric acid, and mercurous nitrate added to remove the silicotungstic acid as the insoluble mercurous salt. Excess mercurous nitrate is oxidised to mercuric nitrate, which is soluble in alcohol and does not interfere with the platinichloride precipitate.

The rubidium in the filtrate is also estimated as platinichloride.

Alkalis in Rock Analysis.—Two methods are available for the general treatment of rocks or ceramics in the determination of their alkali content. The first of these, due to Berzelius, consists in attacking the material with hydrofluoric and sulphuric acids followed by removal of all metals except the alkali group and by conversion of the sulphates to chlorides. The second procedure, that of J. Lawrence Smith, is the one most commonly adopted, and here the substance is decomposed by heating with ammonium chloride and calcium carbonate. It is then only necessary to remove calcium and any sulphate which may have been present.

(*a*) *Lawrence Smith Method.*—The finely powdered sample (1 g.) is intimately mixed with an equal weight of ammonium chloride and with eight times its weight of dense granular calcium carbonate, and heated in a tubular platinum crucible fitted with a cap. The ignition is made very gently at first until no more ammonia is evolved and then strongly for 40–60 minutes. The product is digested with 50 ml. of water in a platinum basin until the solution is saturated with calcium hydroxide, when it is carefully decanted, after settling, through a filter paper. The extraction is repeated three times and the residue and filter paper finally washed with 50–100 ml. of hot water or a hot saturated solution of calcium hydroxide, depending on whether little or much magnesium is present. The combined filtrate is now reduced to 100 ml., filtered if any magnesium separates, and the bulk of the calcium removed with ammonia and ammonium carbonate, double precipitation being used. The last traces of calcium are removed as oxalate and the final liquor evaporated to dryness with a little hydrochloric acid to decompose any alkali carbonate which may have been formed. Ammonium salts are removed by ignition and the alkali chlorides weighed (Hillebrand and Lundell, "Applied Inorganic Analysis," p. 787; van Tongeren, Z. anorg. Chem. 1934, **218**, 252; Lamar, Hazel, and O'Leary, Ind. Eng. Chem. [Anal.], 1935, **7**, 429).

(*b*) *Method of Berzelius.*—In this treatment the mineral, which need not be so finely ground as

for the preceding method, is heated in a small platinum basin with hydrofluoric and sulphuric acids until no gritty particles are felt on stirring with a stout platinum wire. The greater part of the sulphuric acid is then expelled, care being taken to see that all the hydrofluoric acid is removed. The cooled residue is extracted with water, the sulphate removed with barium chloride, and, without *filtering, the mixture is evaporated to dryness* Extraction with hot water is now followed by the addition of barium hydroxide and, in order to render the magnesium precipitate less soluble, again evaporated to dryness without filtering. This residue is now filtered with the aid of a little water and well washed with barium hydroxide solution. Excess of barium is removed with ammonia and ammonium *carbonate, the filtrate evaporated to dryness* and heated gently to remove ammonium salts The residual alkali chlorides are again treated for the removal of barium, taken to dryness, and gently ignited Any traces of magnesium present can either be determined later or can probably be removed with 8 hydroxyquinoline (*see* under Lithium) or as magnesium ammonium phosphate.

The further analysis of the mixed alkali chlorides is then conducted as set out under the separate metals

Other methods, less used than the preceding, employ boric, lead, or bismuth oxides as decomposing agents

Copper.—Copper may be separated from the metals of the later analytical groups by precipitation as sulphide in dilute acid solution Removal of the arsenic group is accomplished by digesting the sulphide with sodium hydroxide and sodium sulphide Hydrogen sulphide precipitates cadmium and bismuth but not copper from solution containing potassium cyanide.

Many organic reagents have been advocated for the determination of copper in the presence of other metals Thus nitroso-β-naphthol quantitatively precipitates copper from very dilute hydrochloric acid solution of the chloride *and sulphate while* Cd, Pb, Hg, Mn, Zn, Ni, and Mg remain in solution.

Salicylaldoxime can also be used to determine copper in the presence of Zn, Ni, Co, $Fe^{\cdots}$, Ag, $Hg^{\cdot\cdot}$, and $As^{\cdots}$ ions. The reagent (1 g. in 5 ml of alcohol and 95 ml. of hot water) is added to a solution of copper slightly acid with acetic acid at room temperature, the precipitate filtered, well washed with water, and dried at 105°. The complex contains 18 95% Cu (Ephraim, Ber. 1930, **63**, 1928) Astin and Riley (J.C S. 1933, 314) state that an alcoholic solution of equivalent amounts of salicylaldehyde and hydroxylamine hydrochloride may replace salicylaldoxime.

ESTIMATION OF COPPER.—(*a*) *As* CuCNS. 150 ml. of a warm or hot sulphuric acid solution containing 0 1 g. of copper is treated with a saturated solution of sulphur dioxide in excess or with 2 g of sodium sulphite. After a short while on a steam bath, most of the free acid is neutralised with sodium hydroxide (any turbidity is cleared with a few drops of acid and a 3–4-fold excess of ammonium thiocyanate in a solution of sulphur dioxide is added. After standing for some hours the precipitate is filtered, washed with cold 1% ammonium sulphate followed by 20% alcohol and dried at 110°.

In the presence of tartaric acid (2-3 g) this method provides a separation from Bi, Sb, Sn, As, Fe, Ni, Co, Mn, Zn, and Cd, but tellurium, selenium, lead, mercury, and the precious metals *interfere (Demorest, Ind. Eng. Chem. 1913*, **5**, 216). If hydroxylamine sulphate, in the presence of much ammonium chloride, is used as reducing agent, then mercury does not interfere (Krauss, Z. angew Chem 1927, **40**, 354).

(*b*) *With Oxine.*—Working in tartrate–sodium hydroxide solutions, copper may be estimated in the presence of most metals excepting Zn, Cd, Mg, and $Fe^{\cdot\cdot}$, while a separation from Cd, Mg, and Be is achieved in acetic acid media

In the former case the copper is precipitated from 0 2*N*-sodium hydroxide containing 5 g of sodium tartrate per 100 ml. of solution while in the latter case the solution contains 5% of sodium acetate and 10% of acetic acid. The reagent is a 2% alcoholic solution and the precipitate is washed with hot water and dried at 110°. $Cu(C_9H_6ON)_2$ contains 18 08% Cu (Berg, Z. anal. Chem 1927, **70**, 341, Calvert, Compt. rend 1932, **195**, 148)

(*c*) *With Quinaldinic Acid*—To 150–160 c c. of the neutral copper solution (0 01 to 0 04 g. Cu) is added 2–5 c c of 2*N* sulphuric acid and the liquid boiled The sodium salt of the reagent (about 4% solution) is then added drop by drop until precipitation is complete After standing for some minutes the green copper quinaldinate is filtered, washed with hot water first by decantation and then on the filter crucible, dried at 125°, and weighed $(C_{10}H_6O_2N)_2Cu,H_2O$ contains 14 96% Cu. This method may be conducted in the presence of Cd, Pb, Mn, Ni, Co, PO_4''', AsO_4''', and AsO_3''' ions (Rây and Bose, Z. anal. Chem. 1933, **95**, 400).

A rapid method of estimating copper is based on the Spacu reaction, that is *the formation* of $Cu(C_5H_5N)_2(SCN)_2$ with pyridine and ammonium thiocyanate (Spacu and Dick, *ibid.* 1927, **71**, 185; Golse, Bull. Soc. chim. 1931, (iv), **49**, 84).

Silver.—The only gravimetric estimation of silver that need be considered is that based on its precipitation as chloride in dilute nitric acid. Lead, cuprous, palladous, mercurous, and *thallous ions interfere as do cyanides* and thiosulphates, while the hydrolysis of antimony and bismuth salts also provides a disturbing feature. The oxidation of univalent copper, mercury, and thallium derivatives prevents their interference and the same process serves to destroy cyanides and thiosulphates. Palladium, antimony, and bismuth can usually be removed by repeatedly dissolving the silver chloride in ammonia and reprecipitating with nitric acid. Bismuth may also be separated by prior precipitation with cupferron. Lead may be removed by depositing silver chloride from dilute solutions; alternatively, lead may be precipitated by ammonium phosphate from a weakly ammoniacal

solution containing ammonium tartrate (Vortmann and Hecht, Z. anal. Chem. 1925, **67**, 276), or as carbonate by passing carbon dioxide into a dilute pyridine solution (Jílek and Kota, Coll. Czech. Chem. Comm. 1933, **5**, 396).

The silver estimation is carried out as follows, care being taken to protect the silver chloride from exposure to light.

The solution, containing about 0·1 g. of silver in 100 ml. of dilute nitric acid (1 : 99), is treated with hydrochloric acid or a soluble chloride at 70° with constant stirring until the precipitant is present in slight excess. The mixture is kept warm until the precipitate settles and is then left for some hours. The silver chloride is filtered on to a filter crucible, washed with 0·01*N*-hydrochloric acid, and dried first at 100° and then at 130°.

G. and P. Spacu have recommended the use of various co-ordination compounds of cobalt and copper for the estimation of silver (Z. anal. Chem. 1932, **90**, 182; Bul. Soc. Stiinte Cluj, *1934*, **7**, *568*).

Gold.—Gold is easily separated from practically all other elements by reduction in hydrochloric acid solution with sulphur dioxide; the interfering elements are selenium and tellurium, which are also precipitated, and lead and the alkaline earths, which give precipitates with the sulphate formed by oxidation of the sulphurous acid. Small quantities of the platinum metals may also be carried down if present in considerable amounts.

Gold may also be easily separated as auric chloride by extracting the latter with ethyl acetate from dilute hydrochloric acid solution; mercuric chloride is also extracted, but can be removed by shaking the extract with 3*N*-ammonium chloride.

After precipitation of the metal, gold may be separated from selenium and tellurium by treating with nitric acid when the last two dissolve. If the reduction is carried out by nitrous acid in a 0·45*N*-HCl solution buffered with Rochelle salt to $p_H>1$, or by ferrous sulphate in 0·3–0·6*N*-hydrochloric acid, then tellurium (and selenium ?) is not reduced (Lenher, Smith, and Knowles, jun., Ind. Eng. Chem. [Anal.], 1934, **6**, 43).

The method of estimating gold by reduction with sulphur dioxide is carried out as follows. The gold solution in about 0·3–0·5*N*-hydrochloric acid, and not containing more than 0·5% of the metal, is treated with considerable excess of saturated sulphur dioxide solution. It is digested for some time on a steam bath, a few millilitres of sulphurous acid added, and allowed to cool. Filtration is effected through a fine filter paper and washing with hot dilute hydrochloric acid followed by hot water. If platinum metals were present the gold is dissolved in aqua regia, evaporated several times to dryness with hydrochloric acid and then reprecipitated either as above or with oxalic acid.

Beryllium.—Most beryllium minerals may be broken down by fusion with sodium carbonate, while a few of the phosphatic rocks can be attacked by aqua regia.

Until comparatively recently beryllium was difficult to separate from other metals and the usual method of determination by precipitating with ammonia in the presence of ammonium chloride or nitrate was unsatisfactory owing to the gelatinous nature of the precipitate and its tendency to adhere to the walls of the vessel.

Moser and his co-workers have, however, evolved a method whereby the hydroxide may be obtained in an easily filtered, compact form. The beryllium is precipitated from neutral solutions by heating with ammonium nitrite and methyl alcohol at 70°, a current of air being passed through the solution. The precipitate is filtered, washed with hot water, and ignited to BeO, as the latter is hygroscopic the crucible should be weighed in a tared weighing bottle.

This method provides a separation from all the metals of the later analytical groups (4, 5, and 6) excepting barium, which should previously be precipitated as sulphate; cadmium and thallium also do not interfere (Moser and Singer, Monatsh. 1927, **48**, 673; Moser and List, *ibid.* 1929, **51**, 181).

For separation from aluminium, chromium, ferric iron, thorium, zirconium and titanium, the above authors recommend the use of tannin, which precipitates these metals from acetic acid solution, whereas beryllium isonly deposited on the addition of ammonia.

A neutral solution (300–500 ml. depending on amount of aluminium, etc., present) containing 30–40 g. ammonium acetate and 20 g. ammonium nitrate is treated with 15–25 ml. of 2*N*-acetic acid. The solution is boiled and enough 10% aqueous tannin, or 3% tannin in saturated ammonium acetate, to precipitate the metals completely is added. The tannin adsorption-complex is filtered by suction, washed with dilute ammonium nitrate solution and dissolved in a little hot dilute sulphuric acid. The resulting solution is neutralised with ammonia and the precipitation repeated. The beryllium in the filtrate is then precipitated by adding ten times as much tannin (in 10% aqueous solution) as there is beryllia present followed by ammonia drop by drop until no more of the complex is deposited. Filtration with suction through a hardened paper is followed by washing with hot water and ignition of the precipitate with the aid of a little nitric acid. The beryllium oxide is weighed using the precautions mentioned above.

In the separation of ferric iron by the preceding method, a little hydrogen peroxide is added to prevent reduction to the ferrous state by the tannin.

The separation of aluminium (and of copper) may be accomplished by precipitation with 8-hydroxyquinoline in weakly acid acetate solution. In the presence of tartaric acid ferric iron can also be removed by this reagent (Kolthoff and Sandell, J. Amer. Chem. Soc. 1928, **50**, 1900; Niessner, Z. anal. Chem. 1929, **76**, 135).

Beryllium can also be separated from ferric, thorium, zirconium, thallous, cupric, chromate, molybdate, arsenite, antimonite, vanadate, tungstate, and uranyl ions by precipitation as basic carbonate with guanidine carbonate in slightly acidic media or in exactly neutral

solution if VO_4''' or WO_4'' is present (Jílek and Kota, Z. anal. Chem. 1932, 89, 345).

Magnesium.—The separation of magnesium from the metals of the first four analytical groups is straightforward, though in the precipitation of aluminium with ammonia and ammonium chloride care must be taken to ensure that the precipitation takes place in exactly neutral solution, otherwise co-precipitation may take place.

The use of 8-hydroxyquinoline (oxine) enables magnesium to be estimated in the presence of the alkali and alkaline earth metals, but double precipitation is necessary when calcium is present or if the magnesium is accompanied by considerable amounts of strontium or barium.

Magnesium is usually separated from calcium by removing the latter as oxalate. It is necessary to add sufficient ammonium oxalate to convert both metals into their oxalates, since the calcium salt is somewhat soluble in magnesium chloride solution. Also reprecipitation is recommended for exact work. This method is unsuitable when the amount of calcium present is very small. In such cases the calcium is precipitated as sulphate from 75% alcohol, although this presupposes the absence of alkali metals with sulphates somewhat insoluble in alcohol. These may be removed by first precipitating the calcium and magnesium as phosphates.

ESTIMATION OF MAGNESIUM WITH 8-HYDROXYQUINOLINE.—The faintly acid boiling solution containing 5–10 g. ammonium acetate is treated successively with a 2% solution of the reagent in 2N-acetic acid and strong ammonia until the solution is alkaline. The precipitate is allowed to settle, filtered through a Gooch or sintered glass crucible, washed with hot water, and dried at 105° or at 130°. At the former temperature the complex is a dihydrate containing 6·98% magnesium; the anhydrous substance obtained at 130° contains 7·78% magnesium. Alternatively the complex may be determined volumetrically (see VOLUMETRIC ANALYSIS, p. 650). If it is desired to reprecipitate, then the precipitate, before drying, is dissolved in the least possible quantity of hydrochloric acid, 2 g. of ammonium acetate added together with a few drops of the reagent and the mixture heated to boiling (Berg, Z. anal. Chem. 1927, 71, 23; Hahn and Vieweg, ibid. p. 122).

If iron and aluminium are present they may be removed by a preliminary precipitation with oxine under slightly acid conditions (p_H 5–6) (Berg, l.c., p. 369; Hahn and Vieweg, l.c.; Javillier and Lavollay, Bull. Soc. Chim. biol. 1934, 16, 1531).

ESTIMATION AS PYROPHOSPHATE.—In this estimation of magnesium, which is not entirely satisfactory, although it has been investigated by many workers, the metal is precipitated as magnesium ammonium phosphate,

$$Mg(NH_4)PO_4,6H_2O,$$

which is subsequently ignited to $Mg_2P_2O_7$. Alkaline earth metals interfere, as also do the alkali metals if present in considerable amounts; reprecipitation will, however, ensure the removal of the latter.

The neutral solution, containing not more than 0·1 g. of magnesia, is treated with a few drops of methyl red followed by 5 ml. of hydrochloric acid (d 1·16), and the volume made up to 150 ml. A saturated solution of diammonium hydrogen phosphate (10 ml.) is added, the solution cooled to 0° and strong ammonia added carefully until neutrality is reached. After stirring for five minutes, a further 5 ml. of ammonia are added, stirring being continued for another 10 minutes, after which the mixture is left for 4 hours. The precipitate is filtered, washed with 0·5N-ammonia, dried, and ignited at 1,000° to constant weight.

Calcium.—Estimation as the oxide, after precipitation as calcium oxalate, is the method most frequently used. It is necessary to remove most other metals though small amounts of barium and moderate amounts of magnesium or alkali metals do not interfere if double precipitation is carried out. No difficulties are experienced in separating the members of the previous analytical groups provided no sulphates, fluorides, or phosphates are present. The usual separations of calcium from magnesium have already been dealt with; others which have been used depend on the precipitation of calcium (a) with ammonium molybdate (see below); (b) with sodium tungstate (Mousseron and Boissou, Bull. Soc. Chim. biol. 1930, 12, 482), (c) with picrolonic acid (Dworzak and Reich Rohrwig, Z. anal. Chem. 1931, 86, 98). These methods may also be used for micro determinations of calcium.

Strontium and barium are usually separated from calcium by taking advantage of the solubility of calcium nitrate in alcohol and ether (1 : 1), concentrated nitric acid or isobutyl alcohol.

In the case of the alcohol–ether mixture, the nitrates, dried at 130°–150°, are crushed in a small basin and extracted with 5 ml. portions of the mixture. After stirring and settling the solution is decanted into a small flask. The number of extractions will depend on the amount of material to be treated, but five should be sufficient. The residue is dissolved in water, evaporated, dried at 150°, and, after crushing, is transferred as completely as possible to a flask using three 5 ml. lots of the solvent. The flask is stoppered, left for 24 hours, and the solution filtered, the residue being washed well by decantation.

In using isobutyl alcohol, the dry nitrates are extracted twice with absolute alcohol (2·5 ml. portions) and then once with 5 ml. of isobutyl alcohol. The residue is dissolved, evaporated, dried, and again extracted with two 5 ml. lots of isobutyl alcohol (Szebellédy, Z. anal. Chem. 1927, 70, 39).

In both cases the calcium is recovered from the filtrate and finally estimated as sulphate. Barium may be separated from calcium and strontium by precipitating as chromate from acetic acid solutions (v. Barium) or as silicofluoride from aqueous alcoholic media.

DETERMINATION OF CALCIUM.—(a) As Oxalate. The slightly ammoniacal solution which should not contain more than about 0·1 g. of CaO per 100 ml. is heated to boiling and

excess of hot 4% ammonium oxalate added with stirring. The mixture is boiled for 2 minutes, kept hot on a steam bath for ½ hour, and then allowed to cool for 2 hours. After filtering, the precipitate is washed with cold 0·1% ammonium oxalate and ignited at 1,200° for 5 minutes. Alternatively the oxalate is converted into sulphate by moistening with redistilled sulphuric acid and, after ignition, weighed as $CaSO_4$.

The estimation may be carried out in the presence of certain other metals, such as silver, lead, iron, aluminium, zinc, etc., if the precipitate is carried out in the presence of citric acid (Erdheim, Rocz. Chem. 1933, **13**, 64).

Brunck (Z. anal. Chem. 1933, **94**, 81) recommends weighing the precipitate as CaC_2O_4,H_2O, in which case it is dried first at 60°–70° and then at 110° or is washed with alcohol and ether.

(*b*) *As Molybdate.* This method provides a clean separation from magnesium with a single precipitation.

A boiling neutral solution is treated slowly (1 drop a second) with 6% ammonium molybdate solution made slightly ammoniacal. When excess of the reagent has been added, the liquor is boiled for at least 10 minutes so that the precipitate may become crystalline when it settles readily giving a clear supernatant liquor. After 30 minutes the molybdate is filtered through a Gooch crucible, the asbestos pad of which has been reinforced with a little ground asbestos, washed with water, dried at 130°, and then ignited in a larger crucible (Ca= 20·03%).

Care should be taken not to add the reagent faster than is recommended or to stir the solution while the precipitate is forming; otherwise the crystals adhere tenaciously to the glass surfaces (Wiley, Ind. Eng. Chem. [Anal.], 1931, **3**, 127).

Strontium.—Whenever possible, strontium is estimated as sulphate. For this purpose, the neutral (preferably chloride) solution is treated with considerable excess (10-fold) of dilute sulphuric acid followed by alcohol equal to the volume of the liquid. The precipitated sulphate is filtered after 12 hours, washed with 50% alcohol containing a little sulphuric acid, then with rectified spirit, dried, and ignited at a dull red heat.

Strontium may also be precipitated as oxalate and ignited to carbonate or oxide. The results are somewhat low, owing to the solubility of strontium oxalate, unless alcohol is added. While such a procedure is legitimate when strontium alone is being determined, it involves the co-precipitation of barium and magnesium if these also are present.

Barium.—The separation of barium from the other alkaline earth metals is usually carried out by the chromate method. Barium chromate is precipitated in the presence either of ammonium acetate (3 g.) or of acetic acid (5 ml.) and ammonium chloride (5 g.). In the former case it is usual to use ammonium dichromate (10% solution) as the precipitant, while in the latter case potassium chromate serves. The barium chromate is dried at 130°; $BaCrO_4$= 54·2% Ba (Skrabal and Neustadl, Z. anal. Chem. 1905, **44**, 742; Szebellédy, *l.c.*).

For the more usual estimation of barium as sulphate, the hot solution (slightly acid with HCl) is treated with a slight excess of hot dilute sulphuric acid and is then kept on a steam bath until the precipitate has settled. The sulphate is filtered, washed with hot water containing a little sulphuric acid and finally with a little water; it is dried and ignited to a constant weight at a dull red heat.

Barium sulphate shows a considerable tendency to carry down barium chloride or nitrate so that it is advisable to treat the ignited precipitate, after weighing, with 1 drop of sulphuric acid, drive off excess acid and re-ignite and weigh (v. Karaoglanov and Sagortschev, Z. anorg. Chem. 1935, **221**, 369; Hahn and Keim, *ibid.* 1932, **206**, 398; Vasilieva, Trans. Kirov Inst. Chem. Tech. Kazan, 1935, Nos. 4–5, 97).

Barium may also be separated from calcium, magnesium, and strontium by adding to 0·5 g. or less of the mixed chlorides, 50–75 ml. of a 4 : 1 mixture of strong hydrochloric acid (33%) and ether. The precipitated barium chloride is washed with the acid-ether mixture (Gooch and Soderman, Amer. J. Sci. 1918, [iv], **46**, 538).

Zinc.—Zinc is best removed from related metals by precipitating as sulphide under carefully controlled conditions. In the prior separation of metals precipitated by hydrogen sulphide in acid solutions it is necessary to have sufficient acid present to prevent zinc sulphide being co-precipitated and, in any case, reprecipitation is recommended in order to avoid loss of zinc at this stage.

Moser and Behr (Z. anorg. Chem. 1924, **134**, 149), using an approximately $N/8$ sulphuric acid solution, find that zinc is completely precipitated by hydrogen sulphide under pressure, whereas such is not the case with manganese, iron, cobalt and nickel. Pressure precipitation is also recommended by Fales and Ware (J. Amer. Chem. Soc. 1919, **41**, 487) who use a solution containing ammonium formate, formic and citric acids. The optimum hydrogen ion concentration corresponds to about a p_H of 2·5, although Jeffreys and Swift (*ibid.* 1932, **54**, 3219) state that precipitation is complete even at p_H 1·6 in media buffered with sulphate–sulphuric acid. The use of the chloroacetic acid-sodium acetate buffer is recommended by Mayr (Z. anal. Chem. 1933, **92**, 166) and at a p_H of 2·6–2·7 the zinc sulphide is granular and uncontaminated by other metals of the ammonium sulphide group except cobalt when present in greater concentrations than 6% (*see also* Frers, *ibid.* 1933, **95**, 1, 113).

Cobalt, however, may be prevented from contaminating the zinc sulphide by precipitating in the presence of gelatin (1–2 mg.) or agar (2–5 mg.) and of acrolein (Caldwell and Moyer, J. Amer. Chem. Soc. 1935, **57**, 2372, 2375).

A separation from magnesium or nickel is obtained by precipitating zinc with cyanamide.

Estimation of Zinc.—(*a*) *As Sulphide* (method of Caldwell and Moyer). The zinc solution, containing not more than 0·25 g. of Zn or 0·5 g. of cobalt and free from chlorides,

is adjusted so that the hydroxides are just not precipitated. Ammonium sulphate (6–8 g.) is added, the solution diluted to 250 ml. and 0·2 ml. acrolein solution added. A rapid stream of hydrogen sulphide is passed for 30 minutes, then 5–10 ml. of a 0·02% gelatin solution are added and the precipitate filtered after 20 minutes. The precipitate is washed with cold water and ignited to the oxide at 1,000° in a muffle furnace. The acrolein solution is made by adding 4 ml. of the aldehyde to 100 ml. water containing 10 mg. of hydroquinone and 1 drop of strong hydrochloric acid.

If cobalt is to be estimated in the filtrate, then the latter is strongly acidified and boiled down to one-third its original volume in order to remove acrolein.

In the method of Mayr, the zinc solution (nitrate or chloride) is treated drop by drop with 2*N*-sodium hydroxide until there is a slight permanent turbidity; 10 ml. of 2*N* chloroacetic acid are added with stirring and, after the solution has become clear, 10 ml of *N* sodium acetate are introduced. The solution is diluted to 150 ml., hydrogen sulphide passed in rapidly for 10–15 minutes, and the zinc sulphide filtered after 15–20 minutes. If other metals are present, the precipitate is washed with 10 ml. of chloroacetic acid and 10 ml of sodium acetate solution in 150 ml. water which has been saturated with hydrogen sulphide and finally with 4% acetic acid saturated with hydrogen sulphide. When zinc alone is present the second wash water only is used.

It is always advisable to convert the sulphide into oxide or sulphate for the purpose of weighing.

(*b*) *As Zinc Ammonium Phosphate.*—To the solution containing about 0·1 g of zinc are added 5 g of ammonium chloride and 10 ml. of 2*N*-sodium acetate. After dilution to 140 ml. it is heated on a steam bath and, when hot, there are added 10 ml. of 10% diammonium hydrogen phosphate. The mixture is heated on the water bath for two hours, filtered, washed first with cold water, and then with alcohol and dried at 105°. The optimum p_H of the solution for maximum insolubility of the precipitate is 6·6. The original p_H of the above liquid is 7·5 but falls to 6·4–6·9 after 2 hours on the water bath (Ball and Agruss, J. Amer. Chem. Soc. 1930, 52, 120).

(*c*) *With Quinaldinic Acid.*—The neutral solution (150 ml) is acidified with 2–5 ml. of dilute acetic acid, heated to boiling, and treated, drop by drop while stirring, with the sodium salt of quinaldinic acid (corresponding to 3–4% solution of the acid). When precipitation is complete, the organic zinc salt is allowed to settle, filtered on to a filter crucible, washed thoroughly with hot water, dried at 125°, and weighed as $Zn(C_{10}H_6O_2N)_2,H_2O$, which contains 15·29% zinc. Manganese, magnesium, the alkaline earth metals, or phosphate do not interfere, while in a slightly ammoniacal solution containing tartrate the precipitation of $Fe^{\cdots}$, Al, Be, Ti, and U is prevented (Rây and Bose, Z. anal. Chem. 1933, 95, 400; 1935, 100, 324).

Cadmium.—From other metals of the hydrogen sulphide group, cadmium may be separated with fair ease. The arsenic group remains dissolved on precipitating with sodium sulphide; lead is precipitated as sulphate, whereas bismuth is usually separated as the basic chloride or nitrate. The solubility of cadmium sulphide in nitric acid forms the basis of a separation from mercury.

The precipitation of cadmium as sulphide is best effected from sulphuric acid solution, a greater concentration of this acid being permissible than is the case with hydrochloric acid. This greater acidity is useful in preventing the precipitation of zinc. Zinc and other metals of the ammonium sulphide group, as well as chromium, aluminium, and magnesium, may be removed by precipitating cadmium with β naphthoquinoline (v. VOLUMETRIC ANALYSIS, p. 654).

The determination of cadmium in alloys of lead, antimony or bismuth can be made by dissolving the alloy (5 g.) in 50 ml of citric acid solution (500 g. to the litre) and 50 ml of 6*N*-nitric acid, the solution then being made distinctly ammoniacal. A saturated solution of potassium cyanide is treated with bromine water until the solution no longer gives a coloration with aqueous sodium nitroprusside and 10 ml of this reagent are added to the above solution. When cold the solution is treated with 10 g. of sodium hyposulphite and the mixture heated to 60° with stirring until the white precipitate has turned black. On cooling, it is filtered with the aid of paper pulp, washed with a solution of 4 g ammonium chloride, 2 g. hyposulphite, and 20 ml. of saturated potassium cyanide in 400 ml of water. The filtrate and washings are saturated with hydrogen sulphide, 20 c.c. of dilute ammonia (1 : 1) added, and hydrogen sulphide again passed in. The precipitated cadmium sulphide is washed with dilute ammonium nitrate, converted to sulphate by warming in a crucible with sulphuric acid and nitric acid, and ignited at a dull red heat (Evans, Analyst, 1929, 54, 404).

Cadmium is never weighed as sulphide owing to the uncertainty of the composition of the compound. When free from contaminating elements the metal may be directly converted to sulphate or, if precipitated as sulphide, it may be transformed to sulphate either by the method given above or by dissolving the precipitate in a little hot dilute hydrochloric acid, evaporating to dryness and treating with sulphuric acid.

The estimation of cadmium as molybdate is carried out as given under calcium, excepting that the precipitation is made from faintly acetic acid solution. The precipitate is ripened by heating just below the boiling-point until it settles readily, after which it is left for 2 hours. The usual precautions must be observed to prevent the precipitate adhering to the glass surfaces. The molybdate, dried at 120°, contains 41·27% Cd (Wiley, Ind. Eng. Chem. [Anal.], 1931, 3, 14).

Mercury.—Generally determined by volatilisation or precipitation of the metal, or volumetrically; separations from other metals are consequently of secondary importance.

In the precipitation with hydrogen sulphide in acid solutions, it is not possible to effect complete separations from zinc or thallium, as these form mixed sulphides with mercuric sulphide. Similar mixed sulphides are also formed with copper, cadmium, and tin (Feigl, Z. anal. Chem. 1924, **65**, 37).

Arsenic and antimony may be removed by digesting the sulphides with hot ammonium polysulphide (not alkaline sulphides). Tin is only partially removed and in its presence some of the mercury dissolves.

A separation of silver and lead is effected by digesting the sulphides with a hot mixture of equal parts of 15% solutions of potassium sulphide and hydroxide. Mercuric sulphide dissolves and is filtered off, the residue being washed with water containing a little of the sulphide-hydroxide mixture. Treatment of the filtrate with 20% ammonium nitrate reprecipitates mercuric sulphide. Cadmium, zinc, or tin sulphide interferes.

The insolubility of mercury sulphide in hot dilute nitric acid ($d=1{\cdot}2$–$1{\cdot}3$) permits the removal of the other members of this group. Chlorides must be absent. The residue is dissolved in aqua regia and any lead sulphate is filtered off or the lead is separated as above.

Mercury may also be separated from many metals by reduction to mercurous chloride or, better, to the metal. According to Willard and Boldyreff (J. Amer. Chem. Soc. 1930, **52**, 569) hydrazine hydrate and stannous chloride are the best reducing agents for the latter purpose, while for the reduction to the mercurous stage hypophosphorous acid in the presence of hydrochloric acid and hydrogen peroxide may be used. Cattelain (J. Pharm. Chim. 1930, [viii], **11**, 580).

Mercurous mercury may be separated from a number of metals by precipitating with cupferron from nitric acid solutions containing not more than $0{\cdot}5N$ of free acid.

A number of complex salts of copper and chromium have also been utilised to estimate mercury. G. Spacu and his collaborators precipitate mercury as $[Cu\,en_2][HgI_4]$ or $[Cu\,pn_2][HgI_4]$, where *en* and *pn* are ethylenediamine and $\alpha\gamma$-propylenediamine respectively. If the first complex is precipitated in the presence of ammonia and sodium potassium tartrate, then Cu, Bi, Pb, $Sn^{\cdot\cdot}$, Al, $Fe^{\cdot\cdot\cdot}$, Mn, Zn, Ni, Co, the alkaline earths, and alkali metals do not interfere (Z. anal. Chem. 1933, **92**, 247; 1932, **89**, 187). Mahr (*ibid.* 1936, **104**, 241) precipitates mercury as $Hg[Cr(CNS)_4(NH_3)_2]_2$, from hot $0{\cdot}1N$-hydrochloric acid solution with freshly prepared Reinecke's salt,

$$NH_4[Cr(CNS)_4(NH_3)_2].$$

The precipitate may be dried at 105° or ignited to Cr_2O_3. It is stated that copper, lead, bismuth, cadmium, arsenic, antimony, tin, and many other metals do not interfere.

ESTIMATION OF MERCURY.—(*a*) *As Sulphide.* The precipitation may be carried out with hydrogen sulphide or better by the hydroxide–sulphide method given above. In this latter method the acid mercuric salt solution (not exceeding 0·1 g. Hg per 100 ml.) is nearly neutralised with sodium carbonate, treated with fresh ammonium sulphide in excess and then with 10% sodium hydroxide, stirring vigorously during the addition, until the mixture becomes pale in colour. It is now heated to boiling, more alkali added until the solution is clear, filtered if necessary and the precipitate washed with warm water containing a little sulphide and hydroxide. The mercuric sulphide is now reprecipitated by adding 25% ammonium nitrate in amount equal to the volume of sodium hydroxide used and the mixture, after boiling to expel ammonia, is filtered and washed successively with hydrogen sulphide water, hot water, alcohol, carbon disulphide, alcohol, and ether. It is dried at 105° and weighed as HgS (Hillebrand and Lundell, *op. cit.*, p. 174).

(*b*) *By Volatilisation of the Metal.*—The estimation of mercury in ores or in small amounts generally is carried out by distillation with quicklime or magnesite in an inert gas; copper strips or copper dust are often added to facilitate decomposition. Alternatively the ore may be heated with iron filings. If present in appreciable amounts, the distilled mercury is collected under water, washed, dried, and weighed. With small quantities the distillation is carried out in a porcelain crucible, having a close-fitting silver or gold lid which is cooled by a small water jacket placed on it. The mercury condenses on and amalgamates with the lid, which is weighed before and after the experiment.

Copper or iron precipitates mercury from acid solutions, the mercury being deposited on the precipitating metal. The mercury is then distilled from the amalgam as above. This method is eminently suitable for small quantities of mercury, while it may also be used for larger amounts if the procedure of Evans and Clarke (Analyst, 1926, **51**, 224) is followed, in which the solution continuously percolates through a bed of copper filings in a small tube.

Boron.—Boron is easily separated from all other elements by volatilisation as methyl borate, $B(OCH_3)_3$, when alkali or alkaline earth borates are acidified and heated with absolute methanol. The resulting ester is estimated by a volumetric procedure (*see* VOLUMETRIC ANALYSIS, pp. 645, 653). When not required to be estimated boron may be removed by evaporating to dryness with hydrofluoric acid or with sulphuric and hydrofluoric acids until fumes of sulphuric acid are evolved.

The methyl borate obtained as above may be collected in a weighed quantity of lime, which forms calcium borate. On ignition, the gain in weight of the lime represents the amount of B_2O_3 in the sample. In this case the acidification of the alkali borate must be made with a little acetic acid (Gooch and Jones, Amer. J. Sci. 1899, [iv], **7**, 34; Moissan, Bull. Soc. Chim. 1894, [iii], **11**, 955).

Aluminium.—Removal of the metals of the first two analytical groups presents no difficulties; the aluminium group is usually precipitated by one of the following methods:

(*a*) *With Ammonia and Ammonium Chloride.* The separation is best accomplished at a p_H of 6·5–7·5, that is, at the colour change of methyl red or rosolic acid. The amount of

ammonium chloride should not be less than 3 g. per 100 ml. of solution, which should be boiled for 2 minutes after precipitation. The precipitate is washed with 2% ammonium nitrate or chloride. Moderate amounts of manganese and nickel do not interfere if phosphates or vanadates are absent, but complete separation is not possible from zinc, cobalt, or copper.

(*b*) *Basic Acetate Method.*—The (preferably) hydrochloric acid solution is neutralised first of all with ammonia and finally with ammonium *carbonate, drop by drop, until a faint permanent* turbidity is obtained which is cleared with one or two drops of hydrochloric acid. If much iron is present the solution is dark red and the end point not easy to determine. The solution is heated to boiling and a slight excess of ammonium acetate (20%) is added. The liquor is boiled for about 3 minutes, filtered hot, and washed with hot water containing 1% of acetate.

The method gives no satisfactory separation from nickel, whereas separation from zinc and *manganese is only complete around a p_H of* 5 2; unfortunately at this acidity the precipitate is not easy to filter.

(*c*) *With freshly precipitated Barium Carbonate.*—The carbonate is shaken with the nearly neutral solution in a stoppered flask for some hours, after which the precipitate is filtered and washed with cold water. After solution in dilute hydrochloric acid, the aluminium is precipitated by method (*a*). Satisfactory separations from manganese, zinc, and ferrous iron are thus *obtained, and also from nickel and cobalt* providing that a little ammonium chloride is added.

The metals of the ammonium sulphide group may be removed by precipitating aluminium with hexamethylenetetramine slightly acidified with sulphuric acid (Kôzu, J. Chem. Soc. Japan, 1935, 56, 22, Râу and Chattopadhya, Z. anorg. Chem. 1928, 169, 99).

Long digestion with "infusible white precipitate," NH_2HgCl, gives a separation of iron and nickel in the presence of chlorides, while *with "fusible white precipitate,"* $HgCl_2,2NH_3$ magnesium, calcium, and manganese may be separated from acid sulphate solutions (Šolaja and others, Arh. Hemiju, 1930, 4, 136).

Separation of Aluminium from Group 3 Metals.—Iron, titanium, zirconium, the rare earths, and manganese give hydroxides insoluble in excess sodium hydroxide and may be thus easily removed. *Magnesium and nickel carry* down aluminium and must be absent, while titanium if present in large amounts is incom*pletely* precipitated.

Iron may be separated from aluminium (*a*) by extracting the ferric chloride with ether from 6*N*-hydrochloric acid, (*b*) by precipitation with ammonium sulphide in ammoniacal tartrate solutions, (*c*) by boiling with sodium thiosulphate when $Al(OH)_3$ is precipitated, (*d*) by precipitation with cupferron in strong acid solutions. The last method *ensures* the removal of V, Zr, Ti, Sn, Nb, and Ta; aluminium is only precipitated if the acidity is less than decinormal.

An excellent separation from Fe, Zn, Cu, Hg, Bi, Ga, and probably many other metals is by precipitation of aluminium as $AlCl_3,6H_2O$, *but alkali salts must be absent.* The hydrochloric acid solution is evaporated to the smallest volume which will keep the salts in solution, cooled, and diluted to 12–25 ml with hydrochloric acid. Saturation of the solution with hydrogen chloride at a temperature not above 15° is followed by the addition of an equal volume of ether and a further treatment with hydrogen chloride. The precipitate is filtered through a Gooch, Munroe, or sintered-glass crucible, washed with HCl+ether (1 : 1), *saturated with hydrogen chloride at 15°,* and either dissolved in water and precipitated with ammonia or ignited to Al_2O_3 by heating at 1,200° under a layer of pure mercuric oxide.

Chromium is easily separated from aluminium by oxidation to chromate with sodium hydroxide and peroxide or ammonium persulphate and a trace of silver nitrate. The aluminium is then precipitated as hydroxide.

8-Hydroxyquinoline separates aluminium from many metals under suitable conditions (*see* VOLUMETRIC ANALYSIS, p 650).

ESTIMATION OF ALUMINIUM.—(*a*) *As Oxide.* Aluminium is precipitated with ammonia and ammonium chloride as indicated above; the hydroxide is filtered, washed, dried, and ignited finally in a blow-pipe flame.

As indicated above, the aluminium may be precipitated by sodium thiosulphate or hexamethylenetetramine.

Aluminium may also be precipitated as basic carbonate from slightly acid solutions by means *of hydrazine carbonate containing free hydra*zine. After precipitation in the cold the mixture is heated on a steam bath for one hour, filtered, washed with warm water or neutral ammonium nitrate solution according as alkali salts are absent or not and ignited to oxide (Jílek and Lukas, Coll. Czech. Chem. Comm 1930, 2, 63).

Gallium.—*Like aluminium and unlike indium,* gallium hydroxide is soluble in sodium hydroxide, but separations by this method from indium, iron, titanium, etc., are not *clean.* E. H. Swift (J. Amer. Chem. Soc 1924, 46, 2377) states that the separation from iron is complete in one operation if the concentration of hydroxide in the solution is 0 3*N*., although the authors (unpublished work) do not find this to be the case if the amount of iron is considerable.

Gallium is advantageously separated from *many metals such as* Pb, Cd, Co, Ni, *etc.*, by precipitation from hot solutions with weak alkalis such as cupric or cuprous oxide, aniline, etc.

Interesting separations of gallium from many metals have been worked out by Moser and Brukl (Monatsh. 1928, 50, 181; 1929, 51, 325) and by Ato (Sci. Papers Inst. Phys. Chem. Res Tokyo, 1930–1936)

Moser and Brukl remove gallium from zinc, nickel, cobalt, manganese, cadmium, beryllium, and thallium by treating the feebly acid solution with ammonium acetate, ammonium nitrate (2% solution), boiling, and precipitating with tannin (10% solution). *The resulting mixture must* contain ten times as much tannin as gallium with a minimum of 0 5 g. The filtered precipitate is washed with 1% ammonium *nitrate*

containing a little acetic acid, dried, and ignited to Ga_2O_3.

Gallium may be precipitated with cupferron (6% solution) from 2*N*- (Moser and Brukl, *l.c.*) or 0·6*N*- (Scherrer, J. Res. Nat. Bur. Stand., 1935, **15**, 585) sulphuric acid. The precipitate is washed with cold dilute sulphuric acid (1–0·5*N*-) and ignited to Ga_2O_3. This method separates from Al, Cr, In, U, and Ce, but not from Sn, Cu, V, Ti, or Zr.

Iron may be removed by precipitating with α-nitroso-β-naphthol (2% in 50% acetic acid) from an acetate-buffered solution (Papish and Hoag, J. Amer. Chem. Soc. 1928, **50**, 2118) or by reducing to ferrous chloride and extracting the gallium trichloride with ether from 6*N*-hydrochloric acid solution.. The trace of iron which always enters the ether is removed with 0·3*N*-sodium hydroxide as above (Swift, *l.c.*).

The methods adopted by Ato depend on the precipitation of gallium with camphoric acid or sodium camphorate (*v. infra*). Indium, thallium, iron, beryllium, titanium, zirconium and thorium interfere, as does aluminium in moderate amounts. Indium may be removed by precipitating with 5% sodium carbonate; the other metals may be separated by extracting gallium chloride with ether.

ESTIMATION OF GALLIUM.—(*a*) *With Ammonia.* Gallium hydroxide precipitated with ammonia alone is difficult to filter, but the presence of sulphur dioxide overcomes this trouble (Dennis and Bridgman, J. Amer. Chem. Soc. 1918, **40**, 1552).

To the gallium solution (0·1 g. in 100–200 ml.), which is preferably acid with sulphuric acid, is added ammonia until faintly alkaline, followed by 5 ml. of 10% ammonium bisulphite solution. Dilute sulphuric acid is added until the solution is just acid to litmus, the solution boiled vigorously for 5 minutes, and the gallium hydroxide filtered after settling. Washing may be done with hot water or with water containing a little neutral ammonium nitrate. The precipitate is ignited finally at a temperature not less than 900°.

(*b*) *With Camphoric Acid.*—The gallium solution (nitrate or chloride) is evaporated to dryness and the residue dissolved in 10 ml. of 6*N*-acetic acid, after which 80 ml. of water and 20 ml. of 10% ammonium nitrate are added. The mixture is placed in a boiling water bath, 2 g. of camphoric acid added and the heating continued for 10 minutes. After cooling the liquor is decanted and the precipitate washed by decantation with a solution made from 80 ml. of water, 5 ml. of 6*N*-acetic acid, and 20 ml. of the ammonium nitrate. The precipitate is transferred to the filter, dried, and heated gently in a porcelain crucible with a flame applied to the upper surface of the residue which melts and begins to burn. When combustion is complete, the filter paper is added and destroyed at moderate temperatures. After ignition the precipitate is weighed as Ga_2O_3.

Indium.—Resembling aluminium and gallium in many respects, indium is, nevertheless, precipitated by hydrogen sulphide in hydrochloric acid solutions up to 0·05*N*-, and partly or wholly precipitated in stronger acid solutions if other precipitable metals are present. It may also be precipitated *from ammonium sulphide–tartrate* solutions and so separated from Al, Zr, Ti, etc.

Indium may be separated from many elements by precipitation of the metal from its salts by boiling with zinc, whereas barium carbonate precipitation may be used to remove fourth group metals.

Ammonia and ammonium chloride quantitatively deposit the trihydroxide $In(OH)_3$ from hot solutions, as also does potassium cyanate. Use of the latter reagent in the presence of ammonium chloride enables indium to be separated from zinc and nickel although re-precipitation is necessary if the ratio of the contaminating metal to the indium is greater than 10. Cobalt may be removed by treating the neutral solution with enough potassium cyanide to dissolve the precipitate first formed and then boiling with a little 10% potassium cyanate, when $In(OH)_3$ is precipitated. Manganese is separated by passing hydrogen sulphide into boiling acetic acid–ammonium acetate solution, while if sulphosalicylic acid and ammonium carbonate are present then aluminium also does not interfere with the deposition of indium sulphide (Moser and Siegmann, Monatsh. 1930, **55**, 14).

Although indium hydroxide is insoluble in alkali hydroxides, while gallium hydroxide is soluble, this property does not supply an entirely satisfactory method of separating the two, even on repetition.

ESTIMATION OF INDIUM.—(*a*) *As Hydroxide.* To the faintly acid solution are added a few drops of methyl orange and then 10% potassium cyanate solution until the colour becomes yellow. The solution is heated to boiling and the hydroxide filtered through paper and washed with hot water. Whether this method is used or precipitation with ammonia and ammonium chloride, it is necessary to wash the precipitate free from chlorides. The hydroxide is dried, ignited at red heat, and weighed as In_2O_3.

Thallium.—Thallium forms well-defined mono- and trivalent salts. In the former state it resembles the alkali metals on the one hand and lead on the other, while in the tervalent state it is related to indium and the heavy metals.

Although not precipitated by hydrogen sulphide in strong acid media, it is carried down by other metals of this group; thallium is only completely precipitated by hydrogen sulphide in acetic acid or ammoniacal solutions, but the resulting thallous sulphide is easily oxidised by air and so filtrations must be rapid and washings done only with dilute colourless ammonium sulphide.

Thallium may be separated from the majority of the metals by extracting thallic bromide in *N*-hydrobromic acid with ether. Gold is also extracted, but is separated by heating the ethereal solution with hot water and adding successively 2 ml. of 10% hydrazine hydrochloride, 2 ml. of 10% potassium cyanide, 2 ml. of 2*N*-potassium hydroxide, and 1 ml. of 5% KI for each 100 mg. of gold and thallium. The latter is precipitated as iodide (Wada and Ishii, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **24**, 135). A separation from second

group metals excepting cadmium is achieved by precipitating thallium with ammonium sulphide in the presence of cyanides.

Lead and manganese are removed by precipitating *them with diammonium hydrogen* phosphate in an ammoniacal solution containing sulphosalicylic acid, while precipitation of thallium, in the filtrate, as chromate removes iron, aluminium, and chromium. If excess of ammonia is present then potassium chromate does not precipitate **Se, Cd, Ni, Zn, Co, Mo,** or **W,** while cyanide prevents the deposition of **Ag, Hg,** and **Cu** (Moser and Brukl, Monatsh. 1926, 47, 709).

Ammonium nitrite–methyl alcohol hydrolysis (*see* Beryllium) removes those metals which are precipitated by this process, although special conditions are necessary for thorium, zirconium, and titanium.

Vanadium is separated from thallium by dissolving the precipitate of thallous metavanadate in the least quantity of strong tartaric acid *solution at 40°, adding ammonia until the colour* becomes blue or is discharged (depending on the amount of vanadium), and precipitating thallium as chromate (Moser and Reif, Monatsh 1929, 52, 343).

ESTIMATION OF THALLIUM.—(*a*) *As Chromate* The ammoniacal thallous solution (thallic salts are reduced with SO_2) is heated to 60°–100° and treated with 2 g of solid potassium chromate for every 100 ml (containing about 0 1 g Tl). *After settling for at least 12 hours, the pre*cipitate is filtered through a Gooch or sintered glass crucible, washed with 1% potassium chromate, then with 50% alcohol, and dried at 120° (percentage Tl = 77 9)

(*b*) *As Cobaltinitrite* —The reagent is made by mixing equal volumes of (*a*) 28 6 g of cobalt nitrate and 50 ml of 50% formic acid in 500 ml water, and (*b*) 180 g of sodium nitrite in 500 ml water. It is added at a temperature of 30°–40° to the thallous solution also at this temperature The scarlet precipitate is filtered, washed with water, and dried at 120°. $Tl_3Co(NO_2)_6$ contains 64 67% *Tl* (Nishuku, J Soc Chem. Ind Japan, 1934, 37, 180B).

The estimation of thallium as thallous iodide, while giving good separations from all metals having soluble iodides, is not strictly quantitative and, *moreover, filtration is slow*

Scandium.—Scandium accompanies the rare earths in analysis, and like them can be separated from other members of the third analytical group by precipitation as oxalate with oxalic acid or as fluoride with hydrogen fluoride. Together with thorium it may be separated from the rare earths by boiling with sodium thiosulphate (*see* Thorium). Thorium may be removed by precipitating it as iodate in strong nitric acid or as fluoride in the presence of much ammonium fluoride, in which medium scandium fluoride is soluble.

Scandium is estimated as Sc_2O_3, after precipitation as oxalate or with ammonium hydroxide (*see* Aluminium).

Rare Earths.—These metals are too nearly related to permit of separations which have a quantitative value, for fractional methods alone can be applied. As a group they are separated from other metals either as oxalates or fluorides or by the insolubility of their double sulphates with alkali sulphates.

Cerium may be separated and estimated fairly readily by virtue of *its conversion into* the quadrivalent state in which its salts are easily hydrolysed. The insolubility of ceric iodate in nitric acid also affords a separation, but not from thorium. Tervalent cerium, however, gives no insoluble iodate.

Cerium may be estimated volumetrically in the presence of most of the rare earths and of thorium. It may also be determined as Ce_2O_3 after precipitation as oxalate or with ammonia. Furthermore, cerous salts with potassium ferrocyanide give at room temperature a precipitate of $CeK[Fe(CN)_6],4H_2O$, which may be weighed as such or heated at 100° to the trihydrate (P. Spacu, Z anal Chem. 1936, 104, 28).

Carbon.—Carbon, whether in organic material, in rocks, or in iron and steel, is nearly always estimated by oxidation to carbon dioxide *by methods given under organic analysis (p. 615).*

Carbonates.—Rapid and moderately accurate determinations may be made by a loss in weight method The carbonate is weighed into a Schrotter flask which is fitted with a stoppered *dropping funnel containing acid to decompose* the carbonate, and an exit tube containing strong sulphuric acid to dry the escaping gas The apparatus is weighed with the acids, etc, after the carbonate has been introduced. The *acid is now run in drop by drop to decompose* the carbonate and the liquid then heated gently to boiling while a stream of CO_2 free dry air is aspirated through it to expel dissolved carbon dioxide The apparatus is cooled and weighed, the loss in weight giving the amount of carbon dioxide in the carbonate

More accurate results are obtained by absorbing the carbon dioxide, after drying, in soda lime or potash and finding the increase in weight of the absorbent The acid used for decomposing the carbonate may be hydrochloric, sulphuric, perchloric, or, preferably, phosphoric acid.

If sulphides are present then the hydrogen sulphide also formed is absorbed either in boiling copper acetate solution acidified with acetic acid or by powdered copper. The latter reagent *is preferred when the ratio of sulphide to* carbonate is great. Hydrochloric acid resulting from the presence of chlorides is efficiently removed by *p* nitrosodimethylaniline (Vernon and Whitby, J S C.I. 1928, 47, 255T; Jacobson and Haught, Ind. Eng. Chem. [Anal.], 1930, 2, 334; Reich-Rohrwig, Z. Anal. Chem. 1933, 95, 315).

Silicon.—Gravimetrically silicon is nearly always estimated as silica. For this purpose the silicate is decomposed, occasionally by acids, generally by fusion mixtures, and the resulting solution evaporated to dryness with hydrochloric or perchloric acid. The *insoluble silica is* weighed and, as it is generally impure, it is volatilised with hydrofluoric acid and sulphuric acid and the residue determined.

Boron is carried down with silica and as it also volatilises with hydrofluoric *acid it must* first be removed as methyl borate (*see* Boron). Tungsten,

niobium, and tantalum also accompany silica, as also may zirconium or titanium, but none of these is volatilised, although with the first-named the final ignition temperature must not exceed 850° (Schoeller and Powell, Analyst, 1928, **53**, 258).

Tin may be separated by dehydrating the silica with perchloric acid, as also may lead, although any lead sulphate can be removed with ammonium acetate.

Fluorine interferes in the estimation of silica due to the formation of volatile silicon fluoride. Losses are inappreciable if the amount of fluorine present is less than 0·3% or if the platinum basin has a good cover and there is an aqueous atmosphere inside during evaporation. The effect of fluorine is minimised by using boric acid or borax in the flux, although this necessitates the subsequent removal of boron.

With large amounts of fluorine the Berzelius method as modified by Hoffman and Lundell (Bur. Stand. J. Res. 1929, **3**, 581) must be used. In this procedure the powdered sample (0·5 g.) is fused at dull red heat with equal parts of sodium and potassium carbonates and the melt extracted with hot water. The insoluble material is boiled with 2% sodium carbonate and the residue retained as part of the silica present. The filtrates are treated with zinc nitrate from 1 g. of zinc oxide, boiled, and filtered from a second silicious residue. Neutralisation of the new filtrate with nitric acid (methyl red as indicator) is followed by evaporation to 200 ml. and the addition of more nitric acid until the solution turns pink. To this is added a reagent made by dissolving 1 g. of zinc oxide, 2 g. ammonium carbonate in 20 ml. of water containing 2 ml. of concentrated ammonia. The mixture is boiled until ammonia is no longer evolved, concentrated to about 50 ml., and diluted with an equal volume of water. The third silicious residue is filtered off, combined with the two previous ones, evaporated to dryness with hydrochloric acid, washed with water containing the same acid (20 : 1), ignited, and weighed.

Small quantities of silica may be estimated by combining silica (1 mol). in dilute acid solution with molybdenum trioxide (12 mols.) and adding *pyramidone* (3 mols.). The insoluble pyramidone silicomolybdate yields a weighable precipitate from very small amounts of silica (King and Watson, Mikrochem. 1936, **20**, 49).

Germanium.—The separation of germanium from other metals is easily carried out by boiling with 6*N*-hydrochloric acid when the volatile germanium tetrachloride distils and may be collected. With a good fractionating column and a current of chlorine, arsenic and antimony, which also form volatile chlorides, may be kept back. If large quantities of arsenic, sulphur, selenium, or tellurium are present, then a second or even third fractionation may be necessary to remove them completely. The germanium is recovered from the hydrochloric acid distillate by means of hydrogen sulphide which quantitatively precipitates white germanium sulphide in 6*N*-acid.

Like arsenic, germanium may be estimated by electrolytic reduction in alkaline solution, using nickel electrodes, and decomposition of the resulting germanium hydrides by heat. The mirror of germanium so formed is compared with standards. Arsenic does not interfere if in the quinquevalent condition. The solution may also be reduced with sodium amalgam (Coase, Analyst, 1934, **59**, 462, 747).

Small quantities of germanium may be determined by converting ammonium germanate to ammonium germanomolybdate and precipitating the insoluble pyridine salt

$$(Py_4H_4[Ge(Mo_2O_7)_6]).$$

ESTIMATION OF GERMANIUM.—(*a*) *As* GeO_2.—The germanium is obtained as sulphide, washed well with 6*N*-sulphuric acid saturated with hydrogen sulphide until free from chlorides, and dissolved in the least quantity of 10*N*-ammonium hydroxide. The solution is collected in a platinum dish and treated with hydrogen peroxide (3%) until oxidation is complete. After evaporation to dryness the residue is moistened with sulphuric acid, gently heated to remove ammonium sulphate and sulphuric acid, and finally ignited at 900°. The ammonium hydroxide should be made from freshly distilled ammonia and the ammoniacal solution should not come into contact with glass, otherwise high results are obtained (Johnson and Dennis, J. Amer. Chem. Soc. 1925, **47**, 790).

(*b*) *As Magnesium Orthogermanate.*—The germanium is obtained in solution as ammonium germanate by the method previously given. Excess of hydrogen peroxide is removed by boiling and the cold solution is made slightly acid with sulphuric acid and diluted to 70–100 ml. depending on the amount of germanium present. To this solution is added 20–25 ml. of 2*N*-ammonium sulphate, 15–25 ml. of *N*-magnesium sulphate, and 15–20 ml. of strong ammonia. After boiling for 2–3 minutes, the mixture is left overnight, the precipitate is filtered, washed with not more than 50 ml. of dilute ammonia (1 : 9), dried, and ignited. It is weighed as Mg_2GeO_4.

Tin.—The sulphides of the copper group (except mercury) may be separated from tin by precipitating them with sodium sulphide. The removal of mercury may be performed by means of ammonium sulphide, or by dissolving the tin sulphide in strong hydrochloric acid; this latter method also serves to remove pentadic arsenic. Arsenic and antimony are best removed by precipitating them as sulphides in the presence of oxalic or hydrofluoric acid. Antimony is also precipitated as sulphide in 16·5% ammonium chloride which is 1·5*N*- with regard to hydrochloric acid (Luff, Chem. Ztg. 1921, **45**, 229, 249, 254, 274).

Unlike antimony, tin can be separated from lead by precipitating the latter as sulphate. Lead, together with copper, zinc, antimony, nickel, cobalt, iron and bismuth, is removed by using phenylarsonic acid, which only precipitates tin; zirconium and thorium are also precipitated.

In the dehydration of the silica it is best to use sulphuric or perchloric acid; nitric acid causes co-precipitation of tin, as the insoluble metastannic acid.

Tin may be separated from fourth group metals by precipitation with ammonia in the presence of ammonium salts, while cupferron may also be used for this purpose; the latter *method also removes aluminium, and chromium*

ESTIMATION OF TIN.—(*a*) *As* SnO_2.—The solution, containing stannic tin, is treated with ammonia and ammonium chloride as described under aluminium and the precipitate is washed with hot 2% ammonium nitrate until chlorides are thoroughly removed The dried precipitate is carefully heated until the paper is charred and finally at 1,100°–1,200°, preferably in a muffle furnace; it is weighed as SnO_2. Ammonium nitrate may be used instead of chloride in the precipitation.

Tin in non ferrous alloys may be converted to dioxide by heating with dilute nitric acid (1 5–2N.) for 2–3 hours at 90°–100° The precipitate is washed with hot water containing *a little nitric acid and ignited as described above* Many elements may, however, contaminate the precipitate. Tin may also be precipitated as the sulphide, which is washed with ammonium nitrate and ignited to oxide, ammonium carbonate facilitates the oxidation.

(*b*) *With Cupferron*.—Metals like copper, lead, tervalent arsenic, and antimony are first removed by precipitating as sulphides in the presence of hydrofluoric acid, and the filtrate (containing 0 1 g. of Sn per 200 ml) is boiled until free from hydrogen sulphide Boric acid (4 g.), concentrated sulphuric acid (2 ml) and hydrochloric acid (5 ml) are added, followed, while stirring, by excess of cold aqueous 10% cupferron. Stirring is continued for about 40 *minutes or until the precipitate becomes compact*, it is filtered through a fine paper, washed with cold water, dried, and ignited as previously described to SnO_2 (Kling and Lassieur, Compt. rend 1920, 170, 1112; Furman, Ind. Eng Chem. 1923, 15, 1071)

(*c*) *With Phenylarsinic Acid*.—From a hot 2·5–5% (by volume) hydrochloric acid or not more than 7 5% sulphuric acid solution (150–200 ml) containing 0 1–0 3 g of tin, the metal is precipitated by adding 35 ml. of saturated aqueous phenylarsonic acid solution. After several hours the precipitate is filtered (with the aid of paper pulp if necessary), washed with 4% ammonium nitrate, and ignited to SnO_2. Good separation is obtained from copper, zinc, lead, antimony, nickel, and cadmium. With iron reprecipitation is necessary, whereas in the case of bismuth the maximum allowable concentration of hydrochloric acid is used to prevent hydrolysis (Knapper, Craig, and Chandler, J. Amer. Chem Soc. 1933, 55, 3945).

Lead.—The precipitation of lead as sulphide from dilute acid solution separates it from the metals of later groups with the possible exception of nickel. For complete precipitation the solution should not be more than 1 4N. with regard to *hydrochloric acid or 0 3N. to nitric* acid. The arsenic group is removed by precipitating with alkali sulphide.

The insolubility of lead sulphate also provides good separations It is necessary to evaporate the solution until fumes of sulphuric appear and at least twice if hydrochloric or nitric acid is present. Silica, tungsten, niobium, tantalum, and the alkaline earth metals interfere, as may also bismuth, antimony, or silver. Silica can be removed by dissolving the lead sulphate in ammonium acetate or better by *treatment* with hydrofluoric and sulphuric acids.

Tungsten, niobium and tantalum are separated by precipitating lead sulphide from acid or alkaline solutions containing tartrate.

Precipitation as bismuthyl salts effects the removal of bismuth or, alternatively, the lead is precipitated as chromate in acetic acid-acetate solution. If ammonium dichromate in nitric acid solution is used, then silver, copper, cadmium, zinc, nickel, manganese, ferric, aluminium, calcium, strontium or barium ions are not precipitated (Karaoglanov and Michov, Z. anal. Chem 1935, 103, 113).

A separation from silver, mercury, cobalt and nickel is obtained when lead is precipitated as *carbonate from dilute pyridine solution (see below)*.

ESTIMATION OF LEAD.—(*a*) *As Sulphate*.—The solution is treated with enough sulphuric acid to provide a fair excess and evaporated down until it fumes After cooling, the sides of the vessel are washed down and the evaporation repeated. Water is now added and, after one hour, the precipitate is filtered through a Gooch crucible, washed with dilute sulphuric acid (3% by volume), and dried by heating slowly to 500°. *If admissible, the dilution of the evaporated solution may be made with aqueous alcohol, as lead sulphate is somewhat soluble in dilute acid*

(*b*) *As Molybdate*.—The neutral lead solution containing about 0 5 g. *lead in 200 ml is treated* with 8 drops of nitric acid, and to the boiling solution is added, drop by drop, a slight excess of 2 5% ammonium molybdate. After boiling for one minute dilute ammonium hydroxide (1 : 2) is added until the liquid is neutral, followed by a few drops of acetic acid. After a few minutes the supernatant liquor is decanted through a Gooch crucible or paper, the precipitate washed with hot 2% ammonium nitrate first by decantation and finally after transferring the precipitate to the paper or crucible. The lead molybdate is dried and ignited at a dull red heat (Weiser, J. Phys. Chem. 1916, 20, 659).

(*c*) *As Carbonate*.—The neutral solution containing not more than 0 2 g. of metal in 80 ml is treated with 5 ml. of alcohol and 15 ml. of 10% aqueous pyridine, after which carbon dioxide is passed in for 45 minutes. The mixture is allowed to stand for 3 hours, carbon dioxide again passed for 5 minutes, the precipitate filtered and washed with water containing 4% alcohol and 0 4% pyridine which is saturated with carbon dioxide. The precipitate may be dried at 120° and weighed as $PbCO_3$, or preferably ignited to PbO (Jilek and Kota, *Coll. Czech. Chem. Comm.* 1933, 5, 396; 1934, 6, 101; Chem. Listy, 1935, 29, 209).

Titanium.—Precipitation with hydrogen sulphide in acid solutions containing tartaric acid serves to separate the copper and arsenic groups, while, if the filtrate is rendered ammoniacal, hydrogen sulphide again passed and about

5 ml. of neutral ammonium sulphite added, then iron, cobalt, nickel, zinc and manganese (partially) are removed. Cupferron quantitatively precipitates titanium in dilute sulphuric acid solution, while aluminium, chromium, phosphorus, nickel, manganese and uranyl salts are not precipitated.

Molybdenum, vanadium, phosphorus, aluminium and beryllium are conveniently removed by precipitating titanium with sodium hydroxide. Beryllium may also be removed by boiling an almost neutral solution with *p*-chloroaniline, when only titania is deposited (Dixon, Analyst, 1929, **54**, 268).

The separation of zirconium and titanium is best accomplished by the method of Powell and Schoeller (Analyst, 1930, **55**, 605). The mixed oxides obtained by hydrolysis of the neutral chlorides with sodium thiosulphate (which removes iron) are fused with ten times their weight of potassium bisulphate and the mass dissolved in 50 ml. of boiling water containing 2–3 g. ammonium oxalate. The solution is neutralised to a faint turbidity with ammonia, one drop of dilute hydrochloric acid added and the solution diluted to 200–250 ml. with 15% ammonium chloride solution. A 10% tannin solution is added drop by drop to the boiling solution in amount sufficient to provide twelve times as much tannin as there is titanium present, the solution being vigorously stirred. The precipitate is collected on a filter paper by gentle suction (a cone being used), washed with hot 12% ammonium chloride, and ignited to titania.

Zirconium (with hafnium), aluminium or thorium is recovered from the filtrate by rendering it weakly ammoniacal, and boiling with excess of tannin. The resulting precipitate is treated as for titanium, but it needs purification by fusion with bisulphate and precipitation with thiosulphate.

Precipitation of titania with guanidine carbonate in tartrate solution removes aluminium, chromate, tungstate, molybdate, uranyl, arsenite or thallous ions (Jílek and Kota, Coll. Czech. Chem. Comm. 1932, **4**, 412).

Separations from niobium and tantalum are given under these metals.

ESTIMATION OF TITANIUM.—(*a*) *With Selenious Acid.*—The cold solution in dilute hydrochloric acid is treated with enough ammonia to reduce the acid below $N/5$ in strength and 5% aqueous selenious acid is added with stirring until the precipitate coagulates. After settling for a few hours the precipitate is filtered with the aid of paper pulp, washed with cold water, dried, and carefully ignited to remove selenium; it is weighed as TiO_2 (Berg and Teitelbaum, Z. anorg. Chem. 1930, **189**, 101). Beryllium, magnesium, aluminium, manganese, nickel, cobalt and the alkaline earths do not interfere. TiO_2 contains 59·95% Ti.

(*b*) *With Tannin and Antipyrine.*—A solution containing not more than 0·1 g. of titania as sulphate is treated with ammonia until the odour persists and the resulting turbidity is cleared with 10 ml. of strong sulphuric acid; 40 ml. of 10% aqueous tannin are added and the solution diluted to 400 ml. To the cooled solution is added 20% antipyrine solution with stirring until the titanium is deposited as a flocculent orange-red precipitate. Stirring is discontinued, but antipyrine is still added until only a white caseous precipitate and no more orange-red precipitate is formed. The mixture is boiled, the flame removed, 40 g. of ammonium sulphate added, and the liquid cooled with occasional stirring. The precipitate is filtered through a paper fitted with a cone and under slight suction. The washing fluid consists of 100 ml. of water, 5 g. of strong sulphuric acid, 10 g. of ammonium sulphate, and 1 g. of antipyrine. After drying at 105° the precipitate is carefully ignited and weighed as TiO_2. Should the original solution have contained alkali metals, the ignited oxide must be washed with hot water, filtered, and re-ignited.

This method is very useful for estimating small amounts of titanium and also provides a separation from Fe, Al, Cr, Mn, Ni, Co and Zn. Phosphates and silicates do not interfere (Moser, Neumayer, and Winter, Monatsh. 1930, **55**, 85).

Zirconium (with hafnium).—These two metals are so closely allied that the separation of the one from the other is only possible by tedious methods of fractionation. The separation of one of them from other metals will also involve the removal of the other.

In the main, zirconium resembles titanium, and methods which serve to separate the latter from contaminating metals will serve for the former also. In addition, zirconium may be precipitated as phosphate from solutions containing 10% by volume of sulphuric or hydrochloric acid. This procedure removes a number of elements, while if hydrogen peroxide is also added titanium does not interfere.

Separations from titanium, niobium or tantalum are listed under these metals. Titanium may also be separated by precipitating zirconium as iodate in 0·3N-sulphuric acid containing hydrogen peroxide (Beans and Mossman, J. Amer. Chem. Soc. 1932, **54**, 1905).

Cupferron quantitatively precipitates zirconium from cold (5°) sulphuric acid solution (10% by volume). The precipitate after washing with dilute hydrochloric acid (1 : 10) is carefully ignited to ZrO_2. A rapid separation from Al, Cr, $UO_2^{\cdot\cdot}$, and small amounts of phosphorus is thus possible.

ESTIMATION OF ZIRCONIUM.—(*a*) *As Phosphate.*—To an approximately 10% (by volume) sulphuric acid solution containing 0·1 g. $Zr(SO_4)_2$ per 200 ml. is added considerable excess (10–100 times) of freshly prepared 10% aqueous ammonium phosphate. The smaller the amount of zirconium present the larger is the excess required. The acidity is now adjusted to 10% by volume and the mixture heated for 2 hours at 40°–50°. If much zirconium is present the precipitate may be filtered after settling, but with small quantities it is better to leave it overnight. Filtration is aided with paper pulp and washing is done with cold 5% ammonium nitrate until excess of phosphate has been removed. After drying, the precipitate and paper are heated carefully until all the carbon has been oxidised and then ignited over a

blowlamp. With small precipitates the zirconium is weighed as ZrP_2O_7, but, owing to the ready hydrolysis of the phosphate, it is better to convert into ZrO_2.

For this purpose the ignited residue is fused with sodium carbonate, the melt extracted with water, and the zirconia after filtration is washed with 1% sodium carbonate, then with water, and ignited.

(*b*) *As Basic Selenite.*—The solution, in approximately 5% by volume of hydrochloric acid (sulphate is undesirable), and having about 0·2 g. of ZrO_2 in 200 ml., is treated with 20 ml of 12·5% aqueous selenious acid and heated to boiling After settling, the precipitate is filtered, washed with hot dilute hydrochloric acid (3 : 97) containing a little selenious acid, dried, ignited, and weighed as ZrO_2.

This method effects a separation from aluminium and the rare earths (cerium must be tervalent), while small quantities of iron (up to 20% of the zirconium) do not interfere if the precipitation is conducted in a more dilute solution (400–700 ml). In this case 30–50 ml. of precipitant are necessary (James and Smith, J. Amer. Chem. Soc. 1920, 42, 1764).

Thorium.—Together with the rare earths, thorium may be separated from other metals by precipitating as oxalate or fluoride. The oxalate is soluble in ammonium oxalate or strong mineral acids and therefore the precipitation should be made by adding oxalic acid to thorium in not more than 0·4*N*-hydrochloric acid. Thorium fluoride is insoluble in dilute mineral acids, but in the presence of the latter the precipitation is more complete if ammonium fluoride be added Considerable excess of this reagent prevents the precipitation of scandium; the latter is also removed by precipitating thorium iodate with excess of potassium iodate in strong nitric acid solution (Meyer, Z. anorg. Chem. 1911, 71, 65) The method also serves for the separation of tervalent cerium, didymium, phosphoric acid, and many common metals, but not of titanium or zirconium. The latter are, however, removed by the oxalate method or by precipitating them as phosphates in dilute sulphuric acid.

Thorium is precipitated with sodium pyrophosphate in a 0·3*N* hydrochloric acid solution, while $Ce^{\cdots}$, La, Pr and Nd are not precipitated.

A separation from the rare earths is also obtained by means of sodium thiosulphate which precipitates thorium (also Sc, Ti, Zr and Al) from boiling solutions The separation is not quite sharp, especially with the yttria group, and repetition of the whole process is necessary. The precipitation is made by treating the neutral chloride solution with two drops of hydrochloric acid, boiling, and adding 2 g. of the reagent. The precipitate is filtered after boiling for 15 minutes and washed with hot water. The filtrate is precipitated with ammonia, the rare earths dissolved in hydrochloric acid, evaporated to dryness, taken up in water, and again treated as above.

Sebacic acid precipitates thorium as sebacate uncontaminated by Ce, La, Pr, Nd, Sa and Gd.

ESTIMATION OF THORIUM.—(*a*) *As Oxalate.*—The thorium (0·1 g. ThO_2 per 100 ml) in 0·3*N*-hydrochloric acid is precipitated from a boiling solution with considerable excess of oxalic acid, left overnight, collected, and washed with a solution of 40 ml. hydrochloric acid and 25 g. oxalic acid in a litre of water. The precipitate is ignited at 1,100° and weighed as ThO_2.

(*b*) *With Sebacic Acid.*—To the boiling neutral solution is added 3–10 ml. of 3% sebacic acid in alcohol with stirring. The voluminous precipitate is filtered, washed with hot water, dried, and ignited to ThO_2. If cerium is present, the precipitate, after drying, is warmed at 100° with fuming nitric acid until no more brown fumes are evolved, the solution is evaporated to dryness, dissolved in 100 ml. of water, and the thorium is reprecipitated as above (Smith and James, J. Amer Chem. Soc. 1912, 34, 281; L. Kaufman, J. Appl. Chem. Russ. 1935, 8, 1520).

Nitrogen.—For the ultimate analysis of nitrogenous materials, *see* the section on organic analysis, p 617.

Ammonium.—ESTIMATION AS PLATINICHLORIDE.—This gravimetric determination is carried out as for potassium, the precipitate being ignited to Pt.

More usually the ammonium compound is heated with caustic alkalis, and the evolved ammonia absorbed in standard acid, excess of which is titrated (*see* VOLUMETRIC ANALYSIS, p 645)

Nitrates.—ESTIMATION WITH NITRON ACETATE.—About 0·1 g. of the nitrate in 100 ml. of water containing a little acetic acid is heated to boiling and 10 ml. of a 10% solution of the base in *N*-acetic acid is added The precipitate is filtered after standing for 24 hours, washed with a little saturated aqueous solution of nitron, dried at 110°, and weighed. The precipitate contains 16·79% NO_3 (Winkler, Z. angew. Chem. 1921, 34, 46).

Nitrites interfere but can be removed by prior treatment with hydrazine sulphate Bromides, iodides, chlorates, perchlorates, chromates and perrhenates interfere, as also do large amounts of chlorides.

Nitrates, nitrites, and many other nitrogen compounds are generally determined by volumetric methods, often after reduction to ammonia. This reduction is usually effected either by a zinc–copper couple or more conveniently by means of Devarda's alloy and alkali. The ammonia is steam distilled into standard acid as in the Kjeldahl method (Devarda, Z. anal. Chem. 1894, 33, 113; Cahen, Analyst, 1910, 35, 307) (*see* VOLUMETRIC ANALYSIS, p. 664).

Phosphorus (as phosphates).—Precipitation of phosphorus as phosphomolybdate is by far the most important method of separating it from other elements. Arsenic, vanadium, titanium, zirconium, silica, organic compounds, and excessive amounts of ammonium salts or mineral acids interfere. Arsenic is co-precipitated when the determination is made at 60°–70°, but not to any great extent at ordinary temperature. Titanium and zirconium in large amounts, or if much phosphate is present, interfere because of the insolubility of their phosphates. They may be removed by fusing any residues with sodium

carbonate or peroxide and extracting the alkali phosphate with water. In the presence of small amounts of phosphate they may, together with vanadium, be removed by means of cupferron. Vanadium as well as arsenic can be separated by heating in hydrogen chloride at 400°–450° (Travers and Lu, Compt. rend. 1933, **196**, 703). Silicon is removed by the usual dehydration method.

Phosphates may also be separated by adding fuming nitric acid and tin to a concentrated nitric acid solution at 86°. The insoluble complex of stannic oxide and phosphoric acid is filtered, washed with hot water, dissolved in caustic potash, and saturated with hydrogen sulphide. Stannic sulphide is removed after acidification of the solution with acetic acid.

Phosphate ions may also be removed by precipitating with slight excess of lead acetate in acetic acid (Bougault and Cattelain, J. Pharm. Chim. 1931, (viii), **14**, 97, 417; Compt. rend. 1931, **193**, 1093) or by excess of solid bismuth oxynitrate in 2–5*N*-nitric acid solution which is finally diluted to 0·5*N*- (Kešans, Latvij. Univ. Raksti, 1929, **1**, 65). These methods provide separations from the common metals of the third to sixth analytical groups. Precipitation as zirconium phosphate may also be used.

Small amounts of phosphorus may be concentrated by adding a little iron or aluminium salt and precipitating either with ammonia or by the basic acetate method. The precipitate is dissolved in nitric acid and the phosphate determined as phosphomolybdate.

Phosphorus in iron and steel is usually determined as phosphomolybdate. If possible the metal or alloy is dissolved in nitric acid, the solution is evaporated to dryness, ignited, and dissolved in hydrochloric acid, boiled, and again evaporated to remove silica. The residue is treated with hot water, silica filtered off, and the filtrate after evaporating to dryness is taken up in nitric acid and phosphate estimated as indicated. Double precipitation may be necessary to remove traces of iron.

Stainless steels which are insoluble in nitric acid must be dissolved in aqua regia or preferably in hydrochloric acid followed by evaporation with nitric acid as recommended by Evans (Analyst, 1929, **54**, 286).

ESTIMATION OF PHOSPHATE.—(*a*) *As Phosphomolybdate.*—The solution containing about 0·05 g. of phosphorus (as orthophosphate) in 100–200 ml. of 5–10% (by volume) nitric acid and 5-15 g. of ammonium nitrate is heated to 50° and a 15–25-fold excess of the reagent added with vigorous shaking or stirring. After some time (depending on amount present or presence of substances such as chlorides or sulphates which delay precipitation) the precipitate is filtered, washed with 5% ammonium nitrate containing a little nitric acid, dissolved in ammonia, and the phosphate precipitated with magnesia mixture. The precipitate of phosphomolybdate is not suitable for direct weighing, as its composition varies somewhat with the conditions of precipitation.

The ammonium molybdate reagent is made by mixing 100 g. of molybdic anhydride with 400 ml. of water and 80 ml. of ammonium hydroxide. After filtering, the solution is poured with agitation into 400 ml. of nitric acid and 600 ml. of water. It is filtered after stirring for 2 hours.

If vanadium is present it may either be kept in the quadrivalent state by means of ferrous sulphate or it may be precipitated as the phosphate in the presence of a large excess of nitric acid.

(*b*) *As Magnesium Pyrophosphate.*—The neutral or weakly acid solution, which must not contain more than 0·2 g. of phosphorus as P_2O_5, is treated with 5 ml. of strong hydrochloric acid, a few drops of methyl-red, and enough water to bring to 150 ml. Acid magnesia mixture is added in 5–10-fold excess the solution cooled in ice, and strong ammonia added with stirring until the solution is neutral. Stirring is continued for 5 minutes, after which a further 5 ml. of ammonia are added, also with stirring. The mixture is left for at least 4 hours, the precipitate filtered and washed with 3–5% (by volume) of ammonia. For the most accurate results the precipitate is dissolved in 50 ml. of warm *N*-hydrochloric acid, diluted to 150 c.c., treated with methyl-red, and 2 ml. of magnesia mixture, and reprecipitated as above. After drying, the precipitate is ignited, carefully at first until the paper is burnt and finally at 1,000° (Epperson, J. Amer. Chem. Soc. 1928, **50**, 321; Hoffman and Lundell, Bur. Stand. J. Res. 1930, **5**, 279; Tananaev and Savtschenko, Ukrain. Chem. J. 1932, **7** (Sci.), 203).

Arsenic.—The outstanding method of separating arsenic from other metals is by distillation of arsenious chloride from hydrochloric acid solution, when, if the distillation is carried out slowly, the only probable contamination is germanium. Numerous reducing agents have been suggested for maintaining the tervalent condition of the arsenic; of these there may be mentioned ferrous sulphate, hypophosphorous or phosphorous acids, hydrazine sulphate and potassium bromide, hydriodic acid or pyrogallol. For appreciable amounts of arsenic it is advisable to pass a current of hydrogen chloride during distillation, in which case a suitable absorption train is necessary.

Arsenic may be separated from many metals by precipitation as pentasulphide from ice-cold 10*N*-hydrochloric acid, or as trisulphide from 9*N*-acid at ordinary temperature. Germanium, molybdenum, mercury, copper, and rhenium interfere, but antimony and tin do not. Precipitation of quinquevalent arsenic with magnesia mixture from cold ammoniacal solutions containing tartrate or citrate also serves to remove antimony, tin or germanium. Large amounts of ammonium salts should be absent, while considerable excess of the reagent is necessary. Washing should be done with dilute ammonium hydroxide.

An excellent separation from antimony is obtained by precipitating arsenate with silver nitrate and estimating the silver in the silver arsenate by Volhard's method (*see* VOLUMETRIC ANALYSIS).

Small amounts of arsenic are usually determined by reducing to arsine and either heating this to form a metallic stain of arsenic or allowing

it to act on dry paper impregnated with mercuric chloride or bromide, when yellow to brown stains are obtained. The results obtained are then compared with standards previously made. Silver nitrate test papers may also be used (v. ARSENIC, Vol. I, pp. 470–471).

Reduction is usually accomplished by means of zinc and dilute sulphuric acid to which very small quantities of ferric alum and stannous chloride are added, and the issuing gas (arsine+hydrogen) is scrubbed free from hydrogen sulphide by means of lead acetate before being allowed to act on the test paper. For the Marsh or metallic stain method, electrolytic reduction is often used (*see* Electrochemical Analysis, p 700).

ESTIMATION OF ARSENIC.—(*a*) *As Trisulphide.*—The strong hydrochloric acid solution (9*N*-) containing only tervalent arsenic is treated with a rapid stream of hydrogen sulphide at room temperature until all the arsenious sulphide is precipitated. Filtered after one hour, it is washed with 8*N*-hydrochloric acid saturated with hydrogen sulphide, then successively with alcohol, carbon disulphide, and alcohol and dried at 105°. It is weighed as As_2S_3. Sometimes a film of sulphide adheres to the glass vessel in which precipitation was carried out, but this can be dissolved in a little ammonia and the sulphide reprecipitated with the acid washing liquor.

(*b*) *As Magnesium Ammonium Arsenate.*—This easy and convenient method suffers from the disadvantage that it is extremely difficult to secure comparable results when the precipitate is ignited to $Mg_2As_2O_7$, for even traces of organic matter or other reducing agents interfere. Many procedures have been advocated for overcoming this difficulty. Furthermore, certain salts have a deleterious effect, while the arsenate is more soluble in the presence of ammonium ions than is the phosphate Dick (Z anal Chem. 1933, 93, 429) has recommended weighing the precipitate as $MgNH_4AsO_4,6H_2O$, and his method is as follows:

The concentrated arsenate solution is treated with 3–5 g of ammonium chloride and 10–15 ml of magnesia mixture. Hydrochloric acid is now added, drop by drop, until the precipitate which has formed is dissolved. To the cold solution is added with stirring one drop of phenolphthalein and enough 2 5% ammonia to turn the solution red, after which an amount of concentrated ammonia is added equal to one-third of the volume of the solution The total volume should now contain not less than 0·1 g of arsenic per 60–70 ml. After cooling in ice water for 1–2 hours the precipitate is filtered through a tared Gooch crucible, washed with 2 5% ammonia followed by alcohol and ether. After drying in a vacuum desiccator it is weighed as $MgNH_4AsO_4,6H_2O$, which contains 25 90% As.

The magnesia mixture is made by dissolving 50 g. of $MgCl_2,6H_2O$ and 100 g. of NH_4Cl in 500 ml of water, adding ammonium hydroxide in slight excess and filtering after 12 hours. The solution is then made just acid and diluted to one litre.

Antimony.—The separation of antimony from metals other than arsenic and tin follows the lines laid down for these elements. Arsenic can be removed by distillation, by precipitation as sulphide from strong hydrochloric acid or as silver arsenate (*see* Arsenic)

Antimony is removed from tin, by precipitating it as sulphide in the presence of tartaric and oxalic acids or of phosphoric acid (Henz, Z. anorg. Chem. 1903, 37, 18; Vortmann and Metzl, Z. anal. Chem. 1905, 44, 532). Henz's procedure is as follows:

The sulphides (not more than 0 3 g of the metals) are dissolved in excess of aqueous caustic potash and 3 g tartaric acid added. Hydrogen peroxide is added in slight excess and the solution boiled for a few minutes, after which a hot solution of 15 g. of oxalic acid is added. When the vigorous action ceases, the solution is again boiled to destroy excess of peroxide, diluted to 100 ml, and hydrogen sulphide passed into the hot solution for 15 minutes after the first appearance of the orange precipitate. It is now diluted to 250 ml, heated, and hydrogen sulphide passed for 15 minutes, after which the flame is removed but the gas still passed for a further 10 minutes The precipitate is filtered on a Gooch crucible, washed first with 1% oxalic acid and then with 1% (by volume) acetic acid, both wash waters being hot and saturated with hydrogen sulphide. The precipitate is then treated as given below.

ESTIMATION OF ANTIMONY —(*a*) *As Sulphide* Sb_2S_3 —The solution in 2*N*-hydrochloric acid is heated to boiling and a rapid stream of hydrogen sulphide is passed in while the liquid is kept at 90°–100°. The flask is gently shaken at intervals and the current of gas decreased as the precipitate darkens. After about half an hour the sulphide is black and crystalline. An equal volume of water is now added and hydrogen sulphide again passed into the hot solution for some minutes. Filtration is through a Gooch crucible, while washing is done with water followed by a little alcohol. The crucible and precipitate are slowly dried at 100°–120° in a current of carbon dioxide and then at 280° for 2 hours. After cooling in carbon dioxide it is weighed as Sb_2S_3 (Vortmann and Metzl, *l c.*; Cahen and Morgan, Analyst, 1909, 34, 3)

Alternatively the precipitate, dried at 100°, may be converted by means of fuming nitric acid and ignition at 800° into the tetroxide, Sb_2O_4

Bismuth.—The separation of bismuth together with other members of the copper group presents no difficulties and is quantitative provided that the concentration of hydrochloric acid present is not greater than about 4*N*- and that the precipitation is carried out at room temperature (Manchot and others, Z anal. Chem. 1925, 67, 177).

Separation from the arsenic group is accomplished by precipitating the sulphide with ammonium sulphide. Alkali sulphides or disulphides cannot be used, as bismuth sulphide is soluble in these though not in the hydrosulphides

The other members of the copper group are usually removed by precipitating the bismuth as oxychloride, oxynitrate, or oxybromide. Moser and Maxymowicz (*ibid.* 1925, 67, 248)

state that the latter method provides the best separation and recommend the following procedure. The nitrate solution, from which any appreciable amounts of chlorides or ammonium salts should be absent, is treated with sodium carbonate solution until the precipitate formed by each drop dissolves only with difficulty on stirring. After dilution to 200–300 ml. there is added 2 g. solid potassium bromate, the solution boiled and any precipitate that remains after boiling is cleared with a few drops of dilute nitric acid. To the boiling solution is added, drop by drop, a 10% solution of potassium bromide until the solution becomes deep brown. The beaker is covered with a clock glass and the solution boiled until most of the free bromine has been expelled and the colour has become a clear yellow. A little more bromide is added and if the colour does not deepen, a little dilute nitric acid is added together, if necessary, with some bromate, so that free bromine shall be present in the solution; this excess of bromine is boiled off, the precipitate filtered through a filter crucible, washed with hot water, and dried at 105°–110°. It is weighed as $BiOBr$ (=68·52% Bi). For more exact work and where much lead is present the precipitate may be dissolved in hot nitric acid and the operation repeated.

Precipitation as oxyiodide has also been recommended, especially for micro-analysis (Strebinger and Zins, Z. anal. Chem. 1927, **72**, 417).

Various organic compounds and certain co-ordination compounds of cobalt give precipitates with bismuth salts in the presence of potassium iodide which may be used for the estimation of bismuth (G. Spacu and P. Spacu, *ibid.* 1933, **93**, 260; Hecht and Reissner, *ibid.* 1935, **103**, 88).

Estimation of Bismuth.—(*a*) *With Cupferron.*—The bismuth solution (about 200 ml.) containing nitric or hydrochloric acid is treated with a 5% cupferron solution until there is present at least three times as much by weight of cupferron as of bismuth. After boiling, ammonia is added until the liquid is alkaline to litmus and then nitric acid to make it just acid. The precipitate is filtered through paper, washed with 0·1% cupferron containing a little nitric acid, and ignited under good oxidising conditions. It is weighed as Bi_2O_3.

This method separates bismuth from cadmium, lead, arsenic, mercury, zinc and quinquevalent antimony (Pinkus and Dernies, Bull. Soc. chim. Belg. 1928, **37**, 267).

(*b*) *With Oxine.*—The nitrate solution containing enough tartaric acid to prevent precipitation on neutralising with ammonia (phenolphthalein) is, after this procedure, made weakly acid with acetic acid. Ammonium or sodium acetate (1–2 g. for each 0·05 g. Bi present) is added, the solution heated to 60°–70°, precipitated with a cold saturated solution of 8-hydroxy-quinoline (oxine) in alcohol or acetone, and the mixture boiled. On cooling, the precipitate is filtered through a crucible, washed with hot water, and dried at 130°. $(C_9H_6ON)_3Bi$ contains 32·60% Bi.

(*c*) *As Oxide.*—The bismuth in nitric acid solution (chlorides and sulphates must be absent) is nearly neutralised with ammonia, the solution diluted to 200 ml. and a saturated solution of ammonium carbonate added in slight excess. The mixture is heated to boiling and then kept on a steam bath for 2 hours. The precipitate is filtered on to paper, washed with hot water and dried. The bulk of the precipitate is removed from the paper on to a watch glass, the residue dissolved in a little nitric acid, and this solution evaporated to dryness in a weighed platinum crucible or dish. The oxide on the watch glass is now added and the whole ignited and weighed as Bi_2O_3.

(*d*) *With Pyrogallol.*—Aqueous pyrogallol is added in slight excess to the boiling acid solution followed by ammonia until alkaline to litmus and then just acidified with dilute nitric acid. After settling, the yellow precipitate is filtered on to a weighed filter crucible, washed with very dilute nitric acid, and then with water, dried at 110°, and weighed as $C_6H_3O_3Bi$ (=62·95% Bi) (Feigl and Ordelt, Z. anal. Chem. 1925, **65**, 448).

Vanadium.—Fusion with sodium carbonate and potassium nitrate followed by extraction with water serves to separate vanadium from many elements. Arsenic, chromium, molybdenum, tungsten, etc., however, accompany vanadium. The vanadium can be separated from chromium, arsenic, sexavalent uranium and phosphorus by precipitation with cupferron (6% solution) in 3–4*N*-sulphuric acid solution. Molybdenum may be separated by precipitation with hydrogen sulphide although it is necessary to have tartaric acid present to prevent co-precipitation of vanadium (*see* Molybdenum).

A good separation from many elements may also be obtained by co-precipitating quinquivalent vanadium with ammonium phosphomolybdate. The precipitation is quantitative if the solution contains at least five times as much phosphorus as vanadium, but in the quadrivalent state vanadium is not precipitated.

Heating at 400° in a current of dry hydrogen chloride causes the volatilisation of vanadium oxychloride. Some of the vanadium may be reduced in the process and so become non-volatile; in this case the residue must be oxidised by evaporating with nitric acid and the process repeated. The oxychloride is collected in water.

Iron and molybdenum may be removed by extraction with ether from cold dilute hydrochloric acid solution; the separation is not complete, as a little vanadium is also extracted. The latter should be in the quadrivalent condition.

Estimation of Vanadium.—Undoubtedly vanadium is best estimated volumetrically, for all the gravimetric methods require that the metal shall be free from interfering elements.

(*a*) *With Mercurous Nitrate.*—To the boiling alkali vanadate solution, which must be free from ammonium salts, but may contain a little nitric acid, is added 3 ml. of 10% hydrogen peroxide and a large excess of mercurous nitrate solution (saturated solution of the salt in hot water). Boiling is continued in a covered beaker for half an hour to destroy excess of peroxide, the precipitate filtered, washed with cold water, dried, and detached from the paper, which is ashed separately, and ignited strongly to the pentoxide, V_2O_5. The purpose of the

hydrogen peroxide is to convert the more soluble hexavanadate, $Hg_4V_6O_{17}$, to a mixture of the insoluble pyro- and ortho- vanadates (Moser and Brandl, Monatsh. 1929, 51, 169).

(*b*) *As Silver Orthovanadate.*—To a neutral alkali vanadate solution containing not more than 0·2 g. of the salt in 200 ml. is added 3 g. of sodium acetate, 0·5 ml. of ammonia (*d* 0·880) and an excess of silver nitrate. The mixture, after heating to boiling, is kept on a steam bath for half an hour, and the supernatant liquor tested for complete precipitation. If a turbidity ensues then the liquid is boiled until clear. After settling, the precipitate is filtered, washed with hot water, dried at 110°, and ignited gently with the crucible inside a larger one. It is weighed as Ag_3VO_4, which contains 11·62% V.

Niobium and Tantalum.—The separation and estimation of these two elements has presented the analyst with great difficulties which have not yet been satisfactorily overcome. The minerals from which they are obtained are complex and the commonly associated elements, titanium, zirconium and tungsten, have many similar analytical properties. These minerals may be attacked (*a*) by hydrofluoric acid with subsequent conversion to sulphates, (*b*) by alkali carbonate or peroxide fusion, or (*c*) by fusion with bisulphate. Subsequent procedure depends essentially on a hydrolytic process whereby the earth acids are precipitated, the contaminating elements being Ti, Zr, W, Sn, Sb, and more or less Fe.

If the hydrolysis is carried out with tartaric acid by the method of Schoeller and Deering (Analyst, 1927, 52, 625), then much of the titanium and zirconium is removed. For this purpose the cold bisulphate melt (containing about 0·2 g. of mixed oxides) is digested with strong tartaric acid solution (3 g.). The solution is diluted to 300 ml., boiled with 30 ml. of strong nitric acid for 15 minutes, and the precipitate filtered with the aid of paper pulp. Washing is done with 1% nitric acid, the precipitate dried and ignited. For a more complete separation the procedure is repeated. The earth acids are not completely precipitated by this method but the residue in the filtrate may be recovered by means of tannin or cupferron. These reagents also precipitate zirconium and titanium, so that tartrate hydrolysis must be repeated on this new precipitate.

Zirconium may also be separated by fusing the mixed oxides with potassium carbonate and extracting the melt with potassium hydroxide solution. The zirconia residue is fused with bisulphate, the product dissolved with ammonium oxalate solution, and any earth acid present is removed by fractional precipitation with ammonia in the presence of tannin. The coloured earth acid complexes are *precipitated first and the ammonia is added* until the white zirconium complex begins to make its appearance. Repetition of the procedure is necessary. The niobium and tantalum in the alkaline filtrate from the extraction of the original fusion with potassium hydroxide are recovered by acidifying with hydrochloric acid and boiling with a small excess of ammonia.

Titanium may be separated from the earth acids by treating the solution with salicylic acid and ammonium oxalate. The oxalate is then precipitated with calcium chloride and the calcium oxalate carries down the niobium and tantalum (Schoeller and Jahn, *ibid.* 1929, 54, 320).

Tungsten may be removed by fusing the oxides with potassium carbonate and treating the aqueous extract of the melt with a slightly ammoniacal solution of a magnesium salt, whereupon the earth acids are precipitated. The process must be repeated for exact results. Further information on these various separations must be sought for in the papers of Schoeller and his co-workers, Analyst, 1921–1936. A complete summary is to be found in Analyst, 1936, 61, 806. *See also* W. R. Schoeller, "The Analytical Chemistry of Tantalum and Niobium," London, 1937.

Separation of Niobium and Tantalum.—For many years the only noteworthy method was that of Marignac, which depended on the relative insolubility of potassium tantalifluoride, K_2TaF_7, as compared with potassium niobium oxyfluoride. More recently Powell and Schoeller (Analyst, 1925, 50, 485) have obtained a fairly quantitative separation by the use of tannin in oxalate solutions.

The weighed oxides (0·25 g.) are fused with bisulphate (3–6 g.) in a silica crucible until a clear melt is obtained. If it does not become clear, the crucible is cooled, 1 ml. of concentrated sulphuric acid added, and the contents again ignited. The fusion is dissolved in 50–100 ml. of saturated (4%) ammonium oxalate and any residue, other than traces of silica, is again treated, its extract being added to the original one. The solution is diluted to 100 ml. for each 0·1 g. of oxides taken, heated to boiling, and treated with freshly made 2% tannin solution. This may produce a permanent turbidity or a precipitate after short boiling; if not then $N/2$ ammonia is added drop by drop until that condition is reached. An orange or reddish colour now shows the presence of niobium in excess, whereas a yellow precipitate indicates that considerable tantalum is present. Tantalic acid is precipitated first, for the oxalo-tantalic compound is stable only in the presence of a certain amount of free oxalic acid, whereas the niobium compound is more stable.

If the liquid is orange coloured, dilute sulphuric acid is added drop by drop until it becomes pure yellow. More tannin is added to a minimum of 0·2 g. with a further 0·1 g. for each 0·03 g. of Ta_2O_5 estimated to be present. A saturated solution of 5 g. of ammonium chloride is added, the liquid boiled for 15 minutes after flocculation has taken place, and filtered with the aid of paper pulp. The precipitate is washed with 2% ammonium chloride and ignited without drying to Ta_2O_5.

The filtrate, containing all the niobium and a little tantalum, is boiled with 5–10 ml. of 2% aqueous tannin and titrated with 0·5N-ammonia until the red solution is decolorised and a precipitate of the same colour is formed. This is heated for some time on a water-bath,

left overnight, collected, washed and dried as above, and then fused for repeated treatment. The fusion is dissolved in ammonium oxalate, tannin added, and 0·5N-ammonia dropped into the boiling solution until the orange colour produced around the drops disappears only slowly. Saturated ammonium oxalate is now added until the yellow precipitate has flocculated and, after digestion on a water-bath, is left overnight, then collected, washed, and ignited. Filtrates are tested for complete precipitation of tantalum by adding a little ammonia, when the precipitate obtained should only be orange-coloured and not yellow.

The niobium is estimated by difference or by complete precipitation of the above filtrates with ammonia until alkaline. The precipitate is treated as above.

Sulphur.—Whenever possible, sulphur is oxidised to sulphate and estimated as such; this also applies to sulphides, sulphites, hyposulphites, metabisulphites, etc. The oxidant generally used for elemental sulphur is a solution of bromine in carbon tetrachloride (up to 60% solution). If necessary the element is first extracted with freshly distilled carbon disulphide, the extract evaporated to dryness, and the residue oxidised to sulphate.

Sulphides.—Sulphides which yield hydrogen sulphide on treatment with hydrochloric acid are decomposed in a flask similar to the Schrötter flask for carbon dioxide, evolved gas being passed through bulbs containing bromine in carbon tetrachloride or hydrochloric acid. To assist in the removal of the gas it is useful to add some granulated zinc or aluminium along with the sulphide while the last traces are removed by boiling and, if necessary, by the simultaneous aspiration of air or hydrogen through the solution. The contents of the bulbs are washed into a beaker, excess of bromine removed, and the sulphuric acid estimated with barium chloride. This method is useful for rapid determinations of sulphur in metallurgical products. Sulphides not decomposed by hydrochloric acid may often be oxidised with aqua regia or with hydrochloric acid and potassium chlorate; if unattacked by such reagents then the material must be fused with sodium peroxide and sodium carbonate, with zinc oxide and carbonate (4 : 1), or by the following method :

Sulphur in Coal and Coke (Eschka's Method).—The finely powdered material (1 g.) is intimately mixed with 2 g. of calcined magnesia and 1 g. of sodium carbonate, and ignited to dull redness in an open platinum crucible for one hour, the mixture being frequently stirred with a platinum wire. Ammonium nitrate (1 g.) is then stirred in and the crucible again heated strongly for 10 minutes. After extraction with water and filtration the sulphate is determined as usual. Alternatively, sodium or potassium carbonate fusion may be employed, but in this case the fusion is extracted with hydrochloric acid containing a few drops of bromine.

Sulphites, Hyposulphites, etc.—These are oxidised to sulphate by means of bromine water, hydrogen peroxide, etc., although, generally they are preferably estimated volumetrically.

Sulphate.—Invariably estimated as barium sulphate yet, in spite of much work on the subject, the precipitation of sulphates is not entirely satisfactory. A certain amount of the precipitant is carried down while excessive washing produces losses due to the appreciable solubility of barium sulphate. For all but the highest accuracy these errors may be considered as cancelling each other. Alkali salts also tend to be co-precipitated, as do ammonium salts. As the latter are volatile and carry away some of the sulphuric acid, they should be eliminated before precipitation. Most other metals may be removed prior to the estimation of sulphate; although if it is not feasible to remove iron then it should be reduced to the bivalent state. For the separation of sulphates from the alkaline earths or magnesium, it is usual to fuse with sodium carbonate, extract the melt with water, filter, and wash the residue with hot 1% aqueous sodium carbonate.

ESTIMATION.—The sulphuric acid solution containing about 0·2 g. per 100 ml. is boiled and 1–2 ml. excess of 10% barium chloride solution added drop by drop with stirring and left overnight. The precipitate is washed efficient first by decantation and then finally on the filter paper with warm water until free from chloride. The paper is dried, charred in a weighed crucible without inflaming, and carbon carefully burnt off under oxidising conditions. The crucible is then heated to about 300°–400° until a constant weight is obtained.

If alkali metals are present the solution of the sulphate should contain a little hydrochloric acid and should be more dilute (not more than 0·05 g. of sulphate per 100 ml.). Furthermore, a larger excess of barium chloride is used (6–7 ml. per 100 ml.) and the precipitant is added quickly. The precipitate may be filtered after settling for half an hour.

If other metals are present the precipitation is carried out in even more dilute solutions and a larger excess of barium chloride is added slowly. It is also advantageous under these conditions to precipitate in the cold and to siphon off the supernatant liquor after 24 hours.

Selenium.—In working with selenium it is essential to remember that appreciable amounts of the element may be lost on warming strong hydrochloric acid solutions of its compounds. No appreciable loss occurs if dilute acid solutions are heated at temperatures below 100°.

Separations of selenium are based almost entirely on either its distillation from hydrochloric acid or its reduction to the element by various reducing agents. By the former method the element may be separated from metals not giving volatile chlorides and also from tellurium. The distillation is made by passing hydrogen chloride through a sulphuric acid solution heated to 300° (Lenher and Smith, Ind. Eng. Chem. 1924, **16**, 837) or by passing carbon dioxide through a phosphoric acid solution containing potassium bromide (Gooch and Pierce, Amer. J. Sci. 1896, (iv), **1**, 181). Geilmann and Wrigge (Z. anorg. Chem. 1933, **210**, 357) state that in the former method some tellurium tends to distil over. The last-named workers separate selenium from Cu,

Bi, Hg, Ag, Au, Ca, Mg, Fe, and the platinum metals by reduction of these metals in alkaline solution with hydroquinone and sodium sulphite, the selenium remaining as sodium selenite. Lead interferes but can be removed by making the solution strongly acid with hydrochloric acid and precipitating selenium with sulphur dioxide.

Under certain conditions hydrazine may be used to separate selenium from Cd, Pb, Bi, Sb, Mo, W and V (Hovorka, Coll Czech Chem. Comm. 1935, 7, 182).

Selenium is usually separated from tellurium by virtue of the fact that the latter is not reduced by sulphur dioxide or hydroxylamine hydrochloride in strong hydrochloric acid solution The following estimations provide for such separations.

ESTIMATION OF SELENIUM.—(*a*) *With Sulphur Dioxide.*—To a solution of the mixed oxides (not more than 0·25 g of each) in 100 ml. of concentrated hydrochloric acid is added while stirring 50 ml of a saturated solution of sulphur dioxide. The red precipitate, after settling, is filtered on to a filter crucible, washed successively with strong hydrochloric acid, cold water, alcohol, and ether. It is essential that both chloride and water be removed. The selenium is dried first at 30°–40° for 3–4 hours and then at 120°–130° for 1–2 hours, cooled in a desiccator, and weighed.

Tellurium in the filtrate is determined by concentrating the solution to 50 ml. at a temperature below 100°, adding 15 ml of saturated sulphur dioxide solution, 10 ml of 15% aqueous hydrazine hydrochloride followed by a further 25 ml of the sulphur dioxide reagent and boiling The precipitated tellurium is filtered, washed first with hot water, and then quickly with alcohol, and dried at 105°.

(*b*) *With Hydroxylamine Hydrochloride.*—The mixed oxides, as above, in 100 ml of solution containing 40–45 ml of concentrated hydrochloric acid are treated with 10 ml. of 25% aqueous hydroxylamine hydrochloride, and heated at 90° for 4 hours. The black selenium deposit is filtered, washed with water and alcohol, and dried at 110°. Tellurium in the filtrate is estimated as in (*a*) Tartaric or citric acids may replace the hydrochloric acid (Lenher and Kao, J. Amer. Chem Soc. 1925, 47, 2454).

(*c*) *In Seleniferous Material containing no Tellurium.*—The material (0·1 g) is fused in a nickel crucible with 3 g. of ferric oxide, 3 g of potassium chlorate, and 4 g of sodium bicarbonate The cold fusion is extracted with water, the filtered solution diluted to 400 ml. and treated with 5 ml. of concentrated hydrochloric acid and 30 g. of hydrazine hydrochloride. The mixture is then boiled in a covered beaker to convert the red modification into black selenium which is filtered, washed, dried and weighed (Benesch and Erdheim, Chem.-Ztg. 1930, 54, 954).

Tellurium.—Like selenium, quadrivalent tellurium is precipitated by hydrogen sulphide in acid solution and if the process has been carried out in the cold, the tellurium sulphide is soluble in alkali sulphide; deposited from hot solutions the precipitate is less soluble, while in the presence of the copper group it is difficult to extract the tellurium completely.

Of the copper group, lead may be removed by evaporating with sulphuric acid to fumes of the latter, diluting and removing the lead sulphate and adding ammonia and ammonium sulphide to the filtrate. The solution is filtered after boiling to remove traces of lead sulphide and the tellurium precipitated by the addition of sodium sulphite. Bismuth is removed as the oxybromide with potassium bromate and bromide (*see* Bismuth, p. 600).

For the separation of mercury the solution is made alkaline with caustic soda, enough sodium sulphide added to dissolve the precipitate, and the solution, after boiling, is treated with solid ammonium chloride until all the mercury is deposited as sulphide. The filtered precipitate is washed with ammonium sulphide and water.

Copper and gold are separated by adding ammonium sulphide to the ammoniacal solution followed by potassium cyanide until the precipitate is dissolved. The solution is boiled and 10–15 ml of a saturated solution of sodium sulphite are added, boiling being continued for 10–20 minutes After dilution to 200–300 ml a little cyanide is added, the solution left for some hours, filtered, and the precipitate washed with a dilute solution of cyanide. The copper or gold is recovered from the filtrate by acidifying and boiling to remove the cyanide

Selenium will accompany tellurium to some extent in the above separations It may be removed by methods already given under that element or, if not to be estimated, it can be separated from the tellurium by treating an alkaline sulphide solution of the two with potassium cyanide until colourless and boiling On addition of 10–20 ml. of saturated aqueous sodium sulphite and further boiling, the tellurium is precipitated and estimated as usual (Brukl and Maxymowicz, Z. anal. Chem. 1926, 68, 14)

ESTIMATION OF TELLURIUM.—(*a*) *With Ammonium Sulphide and Sodium Sulphite.*—The weakly ammoniacal solution is warmed and ammonium sulphide added drop by drop until the precipitate is completely dissolved. A saturated solution of sodium sulphite (20–25 ml) is now added, the solution boiled for 10–20 minutes and diluted to 200–300 ml. It is again boiled with a little more sulphite, allowed to settle for some hours, filtered on to a filter crucible, washed with water, alcohol and ether, and dried at 100°, preferably in nitrogen (Brukl and Maxymowicz, *l.c.*)

(*b*) *As Dioxide,* TeO_2.—The material (elemental tellurium, oxides or tellurites) is dissolved in hydrochloric acid or potassium hydroxide (10%) using 2 ml. per 0·2 g. of oxide. If alkaline the solution is slightly acidified with hydrochloric acid and diluted to 200 ml. with boiling water. Dilute ammonia is added in slight excess and the solution made just acid with acetic acid. The crystalline dioxide separates out on cooling, is filtered on to a crucible, washed with water, and dried at 105° to constant weight (Browning and Flint, Amer. J. Sci. 1909, [iv], 28, 112; Moser and Miksch, Monatsh. 1923, 44, 349). Neutralisation of the solution may also be advantageously carried out with pyridine (Jilek and Kota, Coll. Czech. Chem. Comm. 1934, 6, 398).

Chromium.—Chromium is best estimated volumetrically and therefore its separation from many other elements is of minor importance (*see* VOLUMETRIC ANALYSIS, p. 655). It is easily separated from metals not belonging to the third group and from many of them it can be removed by oxidation to chromate and precipitation of iron, aluminium, etc., by ammonia. The oxidation may be made by means of ammonium persulphate or, more generally, with sodium peroxide. Alternatively, the material may be fused with sodium peroxide or with sodium carbonate and nitre. Vanadium, iron, zirconium, etc., may be removed also by precipitating them with cupferron.

ESTIMATION OF CHROMIUM.—*As* Cr_2O_3.—Most of the gravimetric estimations of this metal deal with its precipitation as $Cr(OH)_3$ followed by ignition to Cr_2O_3. The oxide tends, however, to oxidise to CrO_3, so that high results are obtained unless the ignition is finished in a stream of hydrogen. The following method due to Dorrington and Ward (Analyst, 1930, **55**, 625) gives a more granular product than that produced with ammonia.

The chromium solution (200 ml.) is treated with 5 g. of ammonium chloride and 1 g. of potassium cyanate and after these have dissolved the mixture is slowly heated to boiling. The fine granular precipitate is allowed to settle, the liquid filtered through paper (Whatman, No. 41) and the residue washed once by decantation with hot 2·5% ammonium nitrate solution made faintly ammoniacal. The filtrate is boiled, a few drops of alizarin S added, followed by concentrated hydrochloric acid until the indicator is yellow and then ammonia until it becomes red. The small precipitate is collected on a second filter paper while the main precipitate is washed on to the first paper and further washed with ammonium nitrate. Any film on the beaker is dissolved in a little hydrochloric acid, reprecipitated with ammonia (using alizarin S), and filtered on to the second filter paper. The two papers and precipitates are then ignited wet in a platinum crucible and after removing the carbon the heating is completed over a Méker burner for 10 minutes. Cr_2O_3 contains 68·42% Cr.

Molybdenum.—Molybdenum, belonging to the analytical arsenic group, is precipitated as an insoluble sulphide, MoS_3, from acid solutions. It is not easy to secure a quantitative deposition, partly due to reduction of some of the molybdenum by the hydrogen sulphide and partly to the delaying action of certain salts such as ferric chloride when these are present. The precipitation is best made from a 5% (by volume) sulphuric acid solution, the hydrogen sulphide being rapidly passed into a boiling solution for 15 minutes. After dilution with an equal volume of hot water the gas is again passed for 10 minutes, the mixture boiled for a few minutes and gassed for a further 10 minutes. The sulphide is filtered after one hour and washed with 1% sulphuric acid saturated with hydrogen sulphide. For purpose of estimation it may be ignited to MoO_3 at 450°–500°.

If tungsten or vanadium is present the precipitation is carried out in the presence of tartaric acid, in which case the wash solution also contains 2% tartaric acid.

Molybdenum sulphide may also be precipitated from alkali or ammonium sulphide solutions by the addition of enough sulphuric acid to form a 2% excess. Hydrogen sulphide is passed into the acid solution for 10 minutes, and the sulphide filtered after 2 hours on a water bath.

Formic acid may replace tartaric acid when tungsten is present and has the advantage of being easily removed should it be necessary to make an ammonia precipitation in the filtrate. In this method the alkaline solution is neutralised with 80% formic acid, an excess of freshly made ammonium sulphide added followed by 5 ml. of formic acid per 100 ml. of solution. The sulphide is filtered after allowing to settle on a steam bath and washed with 5% formic acid and estimated as MoO_3 or by one of the methods given below (Koppel, Chem.-Ztg. 1924, **48**, 801; Štěrba-Böhm and Vostřebal, Z. anorg. Chem. 1920, **110**, 81).

Arsenic may be separated from molybdenum by distillation as $AsCl_3$ (*see* Arsenic, p. 599), while antimony may be rapidly removed by boiling a hydrochloric acid solution with sheet lead (Schoeller and Powell, " Analysis of Minerals and Ores of Rarer Elements," 1919).

ESTIMATIONS OF MOLYBDENUM.—(*a*) *As Lead Molybdate.*—The solution, slightly acid with acetic acid, and containing about 0·1 g. of molybdenum per 200 ml., is heated to boiling and treated drop by drop with a 4% solution of lead acetate in 1% (by volume) of acetic acid. A milky solution is obtained which clears somewhat when excess of the lead salt has been added. It is desirable to avoid any considerable excess of precipitant and so the mixture is boiled for a few minutes, allowed to settle, and the clear solution tested by using a fresh tannin solution as external indicator. An excess of 2 ml. of lead acetate is finally run in, the precipitate allowed to settle for about 30 minutes on a steam bath, and the clear liquor decanted through paper or a Gooch crucible. The residue is washed first by decantation, then on the filter, with hot 2% ammonium nitrate. It is ignited at a low red heat and weighed as $PbMoO_4$.

Appreciable amounts of chlorides or sulphates should be absent, but if present the precipitate should be dissolved in hydrochloric acid, neutralised with ammonia as far as possible without producing a permanent precipitate, and excess of ammonium acetate added. A few drops of lead acetate are then added to ensure complete precipitation.

(*b*) *With a-Benzoin Monoxime* (cupron).—The molybdate solution (about 0·1% MoO_3), containing 5% by volume of mineral acid, is precipitated at 5°–10° with a 2% alcoholic cupron solution in slight excess. Bromine water is added until the solution is pale yellow followed by a little more of the precipitant. The precipitate is filtered with the aid of a little paper pulp and washed with an acidified solution of the reagent. It is slowly charred in a platinum crucible, ignited to constant weight at 500° and weighed as MoO_3 (Knowles, Bur. Stand. J. Res. 1932, **9**, 1). Vanadates and

chromates, if present, must first be reduced with sulphur dioxide or ferrous sulphate while antimony does not interfere.

(c) *With Oxine.*—The neutral solution of alkali molybdate is acidified with a few drops of 2*N*-sulphuric acid, 5 ml. of 2*N*-ammonium acetate added, and the liquor diluted to 50–100 ml. A 5% solution of oxine in 4*N*-acetic acid is then added to the boiling solution until the supernatant liquid is perceptibly yellow. After boiling and stirring for a few minutes, the precipitate is filtered on to a filter crucible, washed with hot water until free of the reagent and dried at 130°. It is weighed as $MoO_2(C_9H_6ON)_2$, which contains 23·08% Mo. This method provides a separation from rhenium (Geilmann and Weibke, Z anorg Chem. 1931, 199, 347; Goto, J. Chem. Soc Japan, 1935, 56, 314).

Tungsten.—Easily separated from those metals which are precipitated by sodium hydroxide or the carbonates and which, after fusion with sodium carbonate, are insoluble in water; tungsten is generally eliminated, however, by precipitation of tungstic acid on heating with mineral acids, cinchonine being added to ensure complete deposition Large amounts of alkali salts retard the precipitation.

Separations from molybdenum, niobium, and tantalum are given under these metals, whereas molybdenum may also be removed by heating the oxides at 270° in dry hydrogen chloride, at higher temperatures (about 700°) tungsten is also volatilised In the ordinary course of analysis tungstic oxide tends to separate with silica, precipitation is incomplete but the trioxide so obtained may be recovered by volatilising the silica with hydrofluoric acid

In the estimation of the element in its minerals, the very finely ground material (1 g) is heated successively with hydrochloric acid and aqua regia, the resulting mixture being evaporated to a small bulk and then diluted with hot water (200 ml). After boiling for 30 minutes the precipitation is completed by adding a 10% cinchonine solution in 3–4*N*-hydrochloric acid The tungstic acid is collected on a filter, washed with dilute cinchonine hydrochloric acid solution, and then dissolved in a little ammonia with the addition of some ammonium chloride (1 g.). The solution is filtered, any residue is ignited, fused with sodium carbonate, the fusion extracted with water, and the solution boiled with a little ammonium chloride. The filtrate is acidified, boiled, and any tungsten precipitated with cinchonine which is treated as above, the resulting ammonia solution being added to the main quantity. This ammoniacal liquor is boiled until free from ammonia, diluted to 200 ml, heated with a few ml. of hydrochloric acid, and the tungsten reprecipitated with cinchonine. The precipitate is collected, washed as before, and ignited to WO_3. The trioxide is heated with a few ml of hydrofluoric acid and 2 or 3 drops of sulphuric acid, dried, reignited, and weighed.

The product may still contain molybdenum, which is removed by fusion with sodium carbonate and a little nitre, extracted with water, and the molybdenum separated as sulphide in the presence of tartaric or formic acid (see Molybdenum). The amount of molybdenum trioxide so obtained is deducted from the weight of tungstic oxide.

Estimation of Tungsten.—(a) *With Tannin and Antipyrine.*—To the dilute tungstate solution, containing not more than 0·15 g. WO_3 in 200–300 ml, is added 2–3 ml. of strong sulphuric acid per 100 ml. and 5–8 g. of ammonium sulphate. The boiling solution is treated with sufficient 10% aqueous tannin to provide 3–4 times as much tannin as WO_3, kept on the steam bath for some time, and then allowed to cool to 15°. A 10% antipyrine solution is added with stirring (about 6 g per 1 g of WO_3), the precipitate filtered and washed with a solution containing 5 ml. of sulphuric acid, 50 g of ammonium sulphate, and 2 g of antipyrine per litre. It is then ignited to WO_3. Aluminium, manganese, zinc, cobalt, iron, and chromium do not interfere, although with the last two reprecipitation is advised (Moser and Blaustein, Monatsh 1929, 52, 351).

(b) *With Tannin and Cinchonine.*—The tungstate solution, which should contain alkali chloride and be neutral to phenolphthalein, is treated with a solution of 0·5 g of tannin and sufficient dilute hydrochloric acid to make the solution just acid to litmus The mixture is gently boiled for 5 minutes during which the original colourless precipitate becomes dark and flocculates 5 ml. of 5% cinchonine hydrochloride solution is added to complete the precipitation and the mixture again boiled for 5 minutes After settling for 6 hours it is filtered with the aid of paper pulp, washed with 5% ammonium chloride containing a little tannin (any white turbidity in filtrate being ignored), and ignited to WO_3 (Schoeller and Jahn, Analyst, 1927, 52, 504).

(c) *With Benzidine.*—The neutral tungstate solution containing about 0·3 g. of WO_3 per 200 ml is treated with 10 ml. of 0·1*N* sulphuric acid, boiled, and a 2% solution of benzidine in 1% hydrochloric acid is added (10 ml for each 0·1 g of WO_3) On cooling, the mixed precipitate of benzidine sulphate and tungstate is filtered, washed with a solution containing 10 ml. of the reagent in 300 ml water, and ignited to WO_3 (von Knorre, Ber 1905, 38, 783).

Jílek and his co-workers have elaborated methods of estimating tungsten in the presence of vanadium, using a complex quinine arsenotungstate, and in the presence of stannic tin by means of oxine in the presence of ammonium oxalate (Chem. Listy. 1930, 24, 73; Coll. Czech. Chem. Comm. 1933, 5, 136).

Uranium.—Normally uranium belongs to the analytical ammonia group, being precipitated as ammonium uranate, but precipitation is only complete in the absence of carbon dioxide and vanadium. Sodium hydroxide also quantitatively precipitates uranium, but again carbonates interfere so that no precipitate is given by sodium or ammonium carbonate. This fact enables uranium to be separated from all metals giving insoluble carbonates or hydroxides with alkali carbonate.

Separation from the copper group is achieved

by precipitating these with hydrogen sulphide in the presence of tartaric acid and from the arsenic group by precipitating uranium sulphide with ammonium sulphide. Tartrates and carbonates prevent the precipitation and so the use of either one or other of these permits the removal of Fe, Al, Ti, Zr, Co, Zn, etc.

Iron, vanadium, titanium and zirconium may be separated from sexavalent uranium by precipitation with cupferron in dilute sulphuric acid solution. Reduction of the uranium to the quadrivalent state now permits its precipitation with cupferron, which serves to separate it from aluminium, chromium, manganese and phosphorus. This method also permits of an estimation of U^{iv} in the presence of U^{vi}, a determination which can also be made by precipitating U^{iv} as the insoluble fluoride.

Uranium may also be determined in the presence of vanadium as uranyl pyrophosphate after precipitation as the ammonium phosphate. For this purpose the dilute sulphuric acid solution is treated with twice as much ammonium phosphate as there is U_3O_8 present, the solution boiled, made alkaline with ammonia, and again boiled. The precipitate is filtered, washed with water containing ammonium sulphate, and ignited at low redness to $(UO_2)_2P_2O_7$.

ESTIMATION OF URANIUM.—(*a*) *As* U_3O_8.—To a dilute sulphuric acid solution of uranyl sulphate (not more than 1%) containing no carbon dioxide or organic matter are added a few drops of methyl red and, after boiling, sufficient carbonate-free ammonia to turn the solution yellow. The precipitate is filtered with the aid of paper pulp, washed with 2% ammonium nitrate solution, dried, and ignited in a platinum crucible at as low a temperature as possible until all the carbon is destroyed and then strongly over a Méker burner and in a slanting position to permit free access of air. It is cooled and weighed as U_3O_8 ($U=84{\cdot}8\%$). In many cases it is advisable to estimate the precipitate titrimetrically in order to make certain of its purity (Lundell and Knowles, J. Amer. Chem. Soc. 1925, **47**, 2637).

(*b*) *With Tannin.*—The neutral or faintly acid solution or a suspension of ammonium diuranate is heated to boiling and treated with tannin, followed by sufficient sodium acetate to neutralise any mineral acid, and ammonium chloride or nitrate to flocculate the precipitate. Alternatively a slightly ammoniacal ammonium acetate solution may be added. The precipitate is collected, washed with 10% aqueous ammonium nitrate containing a few drops of ammonia and a little tannin, and ignited, first at a low temperature and finally at 1,000° to form U_3O_8 (P. N. Das-Gupta, J. Indian Chem. Soc. 1929, **6**, 777).

(*c*) *With Oxine.*—The uranyl chloride or nitrate solution made neutral with ammonia is treated with 1–2 g. of ammonium acetate and sufficient acetic acid to give a 5–10% acid solution. After boiling there is added a 5% solution of oxine, the precipitate is filtered on to a filter crucible, well washed with hot water, dried at 110°, and weighed as

$$UO_2(C_9H_6ON)_2,C_9H_7ON,$$

which contains 33·8% of uranium (Hecht and Reich-Rohrwig, Monatsh. 1929, **53**, 596).

For a rapid determination of uranium in carnotite, see J. Ind. Eng. Chem. 1922, **14**, 531.

Fluorine.—Fluorine in rocks and minerals is generally estimated in the filtrate after removing silica by either the Berzelius or Hoffman-Lundell method (see Silicon, p. 594).

In quantitative analysis it is usually separated as calcium fluoride, although the method is not ideal in that the precipitate is slightly soluble. Carnot's method of attacking fluorides with sulphuric acid and silica, absorbing the evolved SiF_4 in concentrated aqueous potassium fluoride, and weighing the precipitated K_2SiF_6, generally gives low results which are stated by Herlemont and Delabre (Compt. rend. 1933, **196**, 1502) to be due to loss as HF. This difficulty is avoided when silica is replaced by ferrosilicon (containing 75% Si) which is much more reactive. Besides weighing as K_2SiF_6 it is also possible to estimate the SiO_2 formed by hydrolysis.

For a rapid estimation of fluorine in glasses, etc., 0·5 g. of the powdered and dried sample is fused with potassium carbonate (6 g.), the melt leached with hot water, filtered, and the residue washed thoroughly. The filtrate and washings are diluted to about 200 ml. and there is added a solution of 1 g. of zinc oxide in 20 ml. of *N*-nitric acid. The mixture is boiled for one minute, filtered, and the precipitate washed with hot water. Fluorine in the filtrate is then determined as below.

ESTIMATION OF FLUORINE.—*As* PbClF.—The neutral or alkaline solution containing 0·01–0·1 g. of fluorine is treated with a few drops of bromophenol blue, 3 ml. of 10% sodium chloride solution, and enough water to make up to 250 ml. Dilute nitric acid is added until the colour is just yellow and then dilute sodium hydroxide until it just changes to blue. Concentrated hydrochloric acid (1 ml.) and lead nitrate (5 g.) are added and the mixture heated on the steam bath until the solid is dissolved, when crystallised sodium acetate (5 g.) is added with vigorous stirring. After digesting on the steam bath for half an hour the precipitate is allowed to settle overnight and filtered on to a filter crucible. It is washed once with cold water, then four or five times with a saturated solution of lead chlorofluoride, then once with cold water, and dried at 120°–150°. PbClF contains 7·26% F (Hoffman and Lundell, Bur. Stand. J. Res. 1929, **3**, 581; Fischer and Peisker, Z. anal. Chem. 1933, **95**, 225). Fluorine may also be precipitated as lead bromofluoride (Vasiliev, J. Appl. Chem. Russ. 1936, **9**, 747).

Chlorine, Bromine and Iodine.—The halogens are usually separated as their silver salts. Cyanides and thiocyanates interfere, but volumetric procedures are available which permit estimation in the presence of these substances. Hydrolysis products of compounds of antimony, tin and bismuth may also contaminate the precipitates, but these metals can be easily removed by precipitation methods. Mercury and chromium which form non-ionised or partially ionised halides must also be separated. Mercuric halides may be triturated

with zinc dust in a little water until no further change takes place, when the halogen may be estimated in the filtrate. Mercurous chloride may be digested with sodium hydroxide, while insoluble halides such as those of silver or lead must be fused with sodium carbonate and the fusion extracted with water. Platinic chloride should be reduced to platinum as it is partially carried down with the silver precipitate.

SEPARATION OF CHLORINE, BROMINE, AND IODINE.—Numerous procedures are available for such separations and they may be roughly divided into three classes. (1) Indirect methods in which it is necessary to secure as many independent relationships as there are radicals present. (2) Differential oxidation whereby iodine is first removed by a mild oxidising agent which will not affect bromides or chlorides, this is followed by the oxidation of bromide to bromine and its removal, leaving chloride to be estimated in the residual liquor (3) Precipitation methods. The only example of this method at present available is the separation and estimation of iodine as palladous iodide

A. ESTIMATION OF CHLORINE AND BROMINE IN MIXTURES OF THE TWO HALIDES —(1) INDIRECT METHODS. (a) The two halides are precipitated as silver salts, filtered on to a sintered glass crucible, washed, dried and weighed *The precipitate is then removed from the crucible* to a beaker with a little water and treated with 50 ml. of 7–8% ammonia which has been run slowly once or twice through the crucible. The silver chloride and some of the bromide dissolves and after occasional stirring for half an hour potassium bromide is added The liquid is warmed to remove most of the ammonia, acidified with nitric acid, and the silver bromide filtered on to the original crucible, washed, dried, and weighed as $AgBr$. The increase in weight multiplied by 3 1531 gives the weight of silver chloride, whence from the weight of the combined silver halides may be found the weight of silver bromide (Longinescu and Pirtea, Bull de Chim. Pure et Appl. 1928, Nos 4–6)

(b) Alternatively, the mixed silver halides may be dissolved in a hot saturated solution of potassium bromide, and reprecipitated as silver bromide by diluting and adding nitric acid (Pirtea, Z. anal Chem. 1934, 96, 263).

(c) Again the weighed silver halides may be reduced with pure zinc and dilute sulphuric acid and the resulting silver either weighed as such or dissolved in nitric acid and estimated. If x is the weight of the mixed halides and y is that of the silver obtained, then the amount of silver bromide present is given by $\dfrac{0\ 75262x-y}{0\ 17818}$ (Bougault and Cattelain, Ann Chim. Analyt. 1932, (ii), 14, 289).

(2) OXIDATION METHODS —(a) *With Telluric Acid.*—0 5 g. of the mixed bromide and chloride and 1 g. of telluric acid are placed in a small distilling flask fitted with a ground stopper carrying a separating funnel the stem of which reaches to the bottom of the flask. Water (40 ml.) is added followed by 10 ml. of sulphuric acid (1 : 1). The mixture is then gently boiled *while a slow current of carbon dioxide is passed* through until the volume is reduced to 17–18 ml. The evolved bromine is collected in sulphurous acid and estimated as $AgBr$, while the chloride in the residue is also determined (Gooch and Cole, Amer. J. Sci 1914, (iv.), 37, 257).

Other oxidising agents which may be used are nitrous acid or ferric sulphate.

(b) *With Hydrogen Peroxide*—The mixed halides in 10 ml. of solution are placed in a separating funnel, covered with 100 ml of light petroleum and treated with a mixture of 5–6 ml of concentrated sulphuric acid and 2–3 ml of hydrogen peroxide. The stoppered funnel is shaken vigorously at intervals for 30 minutes, the aqueous layer removed, and the petroleum layer washed 2–3 times with a little water, chlorine being estimated on the combined aqueous material. The petroleum layer is treated with 40 ml of amyl alcohol and with successive small amounts of sodium until 2 g. has been added, the resulting $NaBr$ being extracted with water. More sodium is then added and the extraction repeated; this procedure is repeated a third time, after which bromine is estimated in the combined aqueous extracts (Longinescu and Prundeanu, Bull Sci Acad Roumaine, 1935, 17, Nos. 3–4, 1)

B. CHLORINE AND IODINE —(1) Of the indirect methods the ones given under A (1) (a) and (b) above are also available here with the necessary modification of the use of potassium iodide instead of bromide The increase in weight ×1 567 gives the weight of silver chloride.

(2) Oxidation methods are numerous, for iodides are easily oxidised to iodine. Nitrous acid, ferric sulphate and potassium iodate are the commonest. The iodine may be collected in cooled aqueous sulphur dioxide or 5% caustic soda. In the latter case if nitrous acid was used hydrogen peroxide is added to the alkaline absorbent in order to oxidise nitrites to nitrates After removal of excess of peroxide the solution is acidified and treated with sulphur dioxide.

(3) *Precipitation of Iodine as* PdI_2 —To a 1% (by volume) hydrochloric acid solution of the alkali halides is added a slight excess of palladous chloride solution and the mixture left for 24–48 hours. The precipitate is filtered on to a tared Gooch crucible, washed with warm water, and then with a very little alcohol. It is sucked dry and heated to 90° for one hour, being weighed as PdI_2. It is somewhat more accurate to heat gradually to 1,000° in a current of hydrogen and weigh as Pd, but the metal must not be allowed to *cool* in hydrogen. It is finally moistened with alcohol, which is then allowed to burn off, cooled in a desiccator, and weighed. Chlorine is determined from the weight of mixed silver halides precipitated from another sample of the original mixture.

C. BROMINE AND IODINE.—(1) (a) Method A (1) (a) can also be used in this case, but it is necessary to employ 25% ammonia to dissolve the silver bromide, the solution being then treated with potassium iodide and nitric acid after removal of most of the ammonia.

(b) The procedure of A (1) (b) is also available, a saturated solution of potassium iodide being *used. The increase in weight* ×3 989 = *weight of* $AgBr$.

(2) Ferric ammonium sulphate or nitrous acid will oxidise iodides and not bromides in acid solution and so the iodine may be removed and estimated. The latter oxidant does not, however, give accurate results if the amount of iodine is small compared with that of bromine present.

(3) The iodine may be determined as palladous iodide.

ESTIMATION OF CHLORINE, BROMINE, AND IODINE.—(1) (*a*) The procedure of A (1) (*b*) and C (1) (*b*) may be combined when all three halides are present. The mixed silver salts ($AgCl+AgBr+AgI$) are treated with hot saturated potassium bromide which converts the $AgCl$ to $AgBr$ so that the resulting precipitate then becomes $AgBr+AgI$. Saturated potassium iodide now converts the bromide to iodide giving the third required relationship (AgL).

(*b*) One of the best indirect methods is that of Bekk (Chem.-Ztg. 1915, **39**, 405), in which the halide solution is divided into two equal parts and each part is precipitated with silver nitrate. The mixed silver halides in one part (0·3–0·4 g.) are washed, dried and weighed ($AgCl+AgBr+AgI$), while in the second they are only washed, after which they are treated with a solution of potassium dichromate (2 g.) in sulphuric acid (30 ml.). The mixture is heated at 95° for 30 minutes and towards the end a slow current of air is blown through the solution. Chlorine and bromine are thus removed while iodide is converted to iodate. The solution is diluted, filtered, made up to about 300 ml., and a strong solution of sodium sulphite added in slight excess, that is until only a faint smell of sulphur dioxide is noticeable after stirring and settling for 10 minutes. The precipitated silver iodide is collected and weighed and the silver in the filtrate and washing is then estimated as iodide. From the three weights so obtained the amounts of each halogen can be calculated:

$$Cl'+Br'+I'+Ag^{\cdot} \rightarrow AgCl+AgBr+AgI \quad (1)$$
$$AgI \rightarrow AgIO_3 \rightarrow AgI \quad (2)$$
$$AgCl+AgBr \rightarrow Ag^{\cdot}+Cl_2+Br_2$$
$$Ag^{\cdot}+I' \rightarrow AgI \quad (3)$$

(2) (*a*) A suitable oxidation procedure is the following. The neutral halide solution, containing not more than 0·25 g. of each of the halides and which should preferably be reasonably free from other salts, is diluted to 700 ml. and treated with 2–3 g. of sodium nitrite and 1·5 ml. of concentated sulphuric acid. The solution is boiled until all the iodine is expelled (about 45 minutes), but the volume of the liquor should not be reduced to less than 500 ml. The iodine is collected in alkaline hydrogen peroxide as under B (2) above, and estimated.

The residual liquid is made faintly alkaline, evaporated to 50 ml., placed in a suitable distilling flask, and neutralised, when cold, with dilute acetic acid (1 : 2), after which there are added 65 ml. in excess and 1–1·5 g. of potassium permanganate. A slow current of steam is passed into the flask until the bromine has been expelled (about one hour), the halogen being collected as in the absorption of iodine.

Chlorine may be estimated in the residual liquor or from the weight of the mixed silver halides as determined in another portion of the original mixture.

Cousin and Dufoùr (J. Pharm. Chim. 1930, (viii), 12, 439) recommend ferric ammonium sulphate or acetic acid and lead peroxide as the oxidising agents.

(3) The halide solution is divided into three portions, in the first of which iodine is estimated as palladous iodide. A second portion is titrated with standard silver solution, while in a third portion chlorine is determined by the method of Stschigol (Z. anal. Chem. 1933, **92**, 420). To this solution (10 ml.) is added 35–40 ml. of 2% aqueous ammonia followed by the exact amount of silver nitrate to react with all the halide as determined on the second portion. The precipitated $AgBr+AgI$ is removed and washed. The filtrate which contains all the chloride is treated with 3–4 g. of sodium carbonate and 15–20 ml. of sodium arsenite solution (8 g. of As_2O_3 and 21 g. of Na_2CO_3 per 100 g. of solution). The liquor is boiled until all the precipitated silver arsenite is reduced to silver, this being filtered off, washed, dissolved in nitric acid, and estimated as usual.

ESTIMATION OF CHLORINE AS SILVER CHLORIDE.—It is preferable to have the halogen in the form of alkali chloride or hydrochloric acid and to dilute the solution until the concentration in respect of chlorine is about 0·05%. With continual stirring there is added a slight excess of silver nitrate solution (0·1–0·3*N*-) containing 1 ml. of nitric acid per litre. The liquor is heated to 60°, tested for complete precipitation, and left for some hours. The supernatant liquor is filtered through a filter crucible, the precipitate washed by decantation with water containing a trace of silver nitrate, transferred to the crucible and again washed with 1% (by volume) nitric acid and finally with water. It is dried first at 100° and then at 130°, or for rapid work the precipitate is washed finally with alcohol and ether, dried at 100°, and weighed as $AgCl$.

The operation should be carried out as far as possible by artificial light.

ESTIMATION OF BROMINE.—The procedure is exactly the same as that for chloride excepting that the precipitate must be freed entirely from nitric acid and that silver bromide is even more sensitive to light than the chloride.

ESTIMATION OF IODINE.—Silver iodide shows a considerable tendency to adsorb any salts, including silver nitrate, which may be present, and therefore precipitation is carried out with very dilute silver nitrate solution (0·5–1%), the iodide solution being correspondingly dilute. Although it is necessary to remove all nitric acid, yet the minimum amount of water to achieve this end should be used. Silver iodide is less sensitive to light than the chloride or bromide.

Hypochlorites and Chlorites.—These may be reduced to chloride with sulphur dioxide, but are best estimated by volumetric methods.

Chlorates.—Chlorates are easily reduced to chlorides and may be determined as such, the common reducing agents being sulphur dioxide, ferrous sulphate or zinc; 0·2 g. of the chlorate

in 100 ml of water is treated with sulphur dioxide and the solution then boiled to remove excess of the gas. The liquid is made slightly acid with nitric acid and silver chloride precipitated as given above In the case of ferrous sulphate there is added to the chlorate solution 50 ml. of a 10% solution of $FeSO_4.7H_2O$, the liquid heated to boiling while stirring and then boiled for 15 minutes. The precipitated basic ferric salt is dissolved with nitric acid and the chloride then estimated in the solution. For the reduction with zinc, excess of this metal is added to the solution which has been made distinctly acid with acetic acid and the mixture boiled for one hour. Unused zinc is dissolved with nitric acid, the liquid filtered and treated with silver nitrate A quicker method is to shake the cold solution acidified with sulphuric acid (10 ml of 50% acid) for 10 minutes with amalgamated zinc (Popov, Ukrain. Chem J. 1935, 10, 413).

Perchlorates. — Perchlorates are usually ignited to chlorides, but losses occur unless the ignition is carried out with the aid of ammonium chloride. 0 2–0 5 g. of the perchlorate is mixed with 2 g. of ammonium chloride in a platinum crucible fitted with a lid The contents are gently ignited for 1½–2 hours and the procedure then repeated. In driving off the ammonium chloride the temperature must not reach the fusing point of potassium chloride, otherwise the crucible is attacked The weight of perchlorate is found either from the loss in weight or by a determination of the resulting chloride Platinum catalyses the decomposition which is only complete in other crucibles when a trace of platinic chloride is added. Perchlorates are not readily reduced to chlorides in aqueous solutions but titanous sulphate has been recommended for this purpose.

Perchlorates which are soluble in alcohol and the metallic radicals of which do not give acetates insoluble in this medium may be estimated by adding a cold saturated solution of potassium acetate in alcohol (8 ml) to the solution of the perchlorate in this solvent. The precipitated $KClO_4$ is collected and dried at 130°. Ammonium salts must be absent (Smeets, Natuurwetensch Tijds 1934, 16, 262)

Mixtures of chlorides, chlorates, and perchlorates may be estimated by determining (*a*) the chloride chlorine, (*b*) reducing with sulphur dioxide or ferrous sulphate from which the chlorate chlorine + chloride chlorine is found, and (*c*) igniting with ammonium chloride, whereby the total chlorine is obtained.

Bromates, Iodates and Periodates — These are most conveniently estimated by volumetric procedures, but they may also be reduced to bromides and iodides and determined as such.

Mixtures of chlorates bromates and iodates may be reduced to the corresponding halides and then estimated by one of the procedures given under the halogens.

Manganese.—It is most usual to estimate manganese by volumetric or colorimetric methods, in which case separations are of secondary importance.

The removal of the first three analytical groups causes no difficulty provided that the aluminium group is precipitated in the absence of elements such as phosphorus or vanadium.

Zinc may be separated by precipitation as sulphide from acetic or formic acid solutions, while nickel is removed with dimethylglyoxime. Cobalt may be precipitated either as potassium cobaltinitrite or by means of phenyl thiohydantoic acid.

Manganese can also be separated from a large number of elements by precipitation as dioxide by nitric acid and potassium chlorate. The solution, which should preferably contain only nitrates, is evaporated to a syrup, diluted with 100 ml of nitric acid, and the liquid boiled in a covered beaker for a few minutes, after which 5 g of potassium chlorate are added in small portions Boiling is continued until the volume has reached 25 ml, when 40 ml of cold water are added and the solution cooled rapidly. The dioxide is filtered and washed either with cold colourless nitric acid or with distilled water at 0°.

Precipitation of manganese with ammonium sulphide provides a good separation from the alkalis and alkaline earths.

ESTIMATION OF MANGANESE —No gravimetric estimation is satisfactory, but where such a procedure is desirable the ammonium phosphate method is generally recommended.

(*a*) *As* $Mn_2P_2O_7$ —200 c c of the acid solution, not stronger than 0 1% with regard to manganese, is treated with 20 g of ammonium chloride and 1–2 g of ammonium phosphate and then heated to boiling Any precipitate is cleared with hydrochloric acid and dilute ammonia added drop by drop with stirring When the precipitate begins to form the addition of alkali is suspended until on stirring the phosphate becomes crystalline This alternate addition of ammonia and stirring is continued until no more precipitate is formed, the solution being boiled the whole time. A further addition of 0 5 ml. of ammonia is made and the solution then cooled to 0° and left for 2 to 3 hours The manganese ammonium phosphate is filtered on to paper, washed with hot 1% ammonium phosphate, and finally with 60% alcohol It is dried, carefully ignited at low temperature until all carbon is oxidised, and finally at 1,000° $Mn_2P_2O_7$ contains 38 70% Mn (Gooch and Austin, Amer. J. Sci 1898, [iv], 6, 233; Nuka, Latvij. Univ Raksti, 1931, 2, 1)

Rhenium.—For analytical purposes rhenium is usually converted into the heptadic per-rhenate ($HReO_4$); if the metal is in a lower state of valency it is easily oxidised either with alkaline hydrogen peroxide or, in the case of insoluble products, by fusion with sodium carbonate and peroxide.

Rhenium belongs to the second analytical group and forms a sulphide Re_2S_7 in strong acid solution (3–4*N*-). It is easily separated from most elements by taking advantage of the sparing solubility of the potassium, silver, and thallium per-rhenates or of the great solubility of the sodium salt.

The most important separation required is that from molybdenum, with which it is frequently associated in nature (*e g.* molybdenite). A moderately complete separation from considerable amounts of molybdenum is

achieved by distilling the rhenium from sulphuric acid (80%) heated at 180°–200°, and into which hydrochloric acid is distilled. The rate of distillation of the rhenium is somewhat slow and it is necessary to replenish the hydrochloric acid by passing in hydrogen chloride during the process. The acid distillate is adjusted to 3–4*N*- and rhenium sulphide precipitated with hydrogen sulphide (Geilmann and Weibke, Z. anorg. Chem. 1931, **199**, 120).

A more complete separation (99%) is afforded by precipitating molybdenum as 2:2′-dipyridyl molybdate (unpublished work).

In either case the last traces of molybdenum are removed by precipitating with oxine as given under Molybdenum. Rhenium in the filtrate is estimated with nitron.

ESTIMATION OF RHENIUM.—*As Nitron Perrhenate.* As separation with hydrogen sulphide often precedes this estimation, this precipitation will also be described:

The solution of septavalent rhenium containing 30–35 ml. of concentrated hydrochloric acid per 100 ml. of solution is heated to 90°–95° and hydrogen sulphide passed in for 2–2½ hours. The black sulphide is then filtered on to an asbestos pad in a tube resembling an Allihn tube, washed with 5% hydrochloric acid saturated with hydrogen sulphide, and then the pad and precipitate pushed with a glass rod into the vessel in which the precipitation took place and from which it is unnecessary to remove all the precipitate. The tube is washed out with water, then with a little water containing 1 ml. of sodium hydroxide and 2 ml. of hydrogen peroxide (30%) to remove the last traces of sulphide, and finally with more water. These washings are run on to the bulk of the precipitate and 2 ml. of sodium hydroxide and 3–4 ml. of peroxide are further added. The covered vessel is set aside for 2–3 hours during which time the sulphide is oxidised to per-rhenate, the liquor boiled to remove excess of peroxide, filtered, and filtrate and washings evaporated to a few ml. The residual liquid is filtered through a small funnel, washed, and the filtrate made up to 50–70 ml. It is neutralised and an excess of 1 ml. of 2*N*-sulphuric acid added, heated to 60°, and freshly filtered 5% nitron acetate added to provide a solution estimated to contain 0·3–0·4% of free nitron (8 ml. of reagent for 0·1 g. of Re in 50 ml. of solution). The mixture is cooled in ice for 2 hours with occasional stirring and filtered on to a filter crucible, the cold filtrate being used to transfer the precipitate. Washing is done with 10–20 ml. of ice-cold 0·3% nitron acetate solution in 3–5 lots and finally with 2–3 ml. of an ice-cold saturated solution of nitron per-rhenate. The precipitate is dried at 110° for 2 hours and weighed as $C_{20}H_{16}N_4HReO_4$ (Re=33·06%) (Geilmann and Voigt, Z. anorg. Chem. 1930, **193**, 311; 1931, **195**, 289; Geilmann and Weibke, *l.c.*).

Iron.—Precipitation with hydrogen sulphide in acid solution removes the members of the first two analytical groups, after which iron may be separated from aluminium, vanadium, tungsten, and similar elements by precipitation by sodium hydroxide. The filtration of ferric hydroxide is aided by the addition of macerated paper pulp.

Aluminium, chromium, titanium, etc., are removed by precipitating iron as sulphide with ammonium sulphide in the presence of ammonium tartrate. Zinc, nickel and cobalt are also precipitated but may be separated by the basic acetate process or by precipitation with ammonia and ammonium chloride. Hexamethylenetetramine may be used instead of ammonia and moreover gives a more easily filtered product, although nickel in any appreciable amounts is not completely separated. Pyridine or hydrazine hydrate also serve to precipitate the hydroxide.

Iron may be estimated in the presence of Cu, Sr, Ba, Ni, Co, Zn, Al, Cr, Cd and Cu by means of the sodium salt of bis-*p*-chlorophenylphosphoric acid, $(ClC_6H_4)_2PO_4H$ (Zetzsche and Nachmann, Helv. Chim. Acta, 1926, **9**, 420, 705, 979).

Where it is objectionable iron may be removed as ferric chloride from many elements by extracting with ether.

ESTIMATION OF IRON.—*As* Fe_2O_3. Although iron may be precipitated with ammonia as given under aluminium, better precipitates are obtained by using hexamethylenetetramine or hydrazine hydrate; the iron must be in the ferric condition.

(1) *With Hexamethylenetetramine.*—To the cold, faintly acid solution of ferric salt (about 0·1 g. Fe in 100–200 ml.) is added 20 g. of ammonium chloride followed by excess of 10% aqueous hexamethylenetetramine with stirring. After settling, the liquor is decanted through a filter paper, the precipitate washed with hot water, transferred to filter, and again washed. Any precipitate adhering to the vessel is dissolved in a few drops of hydrochloric acid and precipitated by ammonia. The ferric hydroxide is ignited at red heat to Fe_2O_3 (Kollo, Bul. Soc. Chim. România, 1920, **2**, 89; 1924, **6**, 109; Rây and Chattopadhya, Z. anorg. Chem. 1928, **169**, 99; Hanuš and Voříšek, Chem. Listy, 1935, **29**, 288).

(2) *With Hydrazine Hydrate.*—To the iron solution are added 2 g. of ammonium chloride and enough ammonia to turn methyl red to yellow. The boiling solution is treated with a slight excess of 4% hydrazine hydrate solution and boiling is continued for a few minutes. The filtered precipitate is washed with hot water containing 1 g. of ammonium chloride and 1 ml. of hydrazine hydrate per 100 ml. and then with hot water. It is finally ignited to Fe_2O_3 (Jílek and Vicovský, Coll. Czech. Chem. Comm. 1931, **3**, 379).

(3) *With α-Nitroso-β-naphthol.*—The reagent in 50% acetic acid is added to the ferric solution which is successively neutralised with ammonia and reacidified with hydrochloric acid. The green precipitate must be ignited in an open crucible to Fe_2O_3 (Burgess, Z. angew. Chem. 1896, **9**, 596).

(4) *With* p-n-*Butylphenylarsinic acid,*

$$C_4H_9{\cdot}C_6H_4{\cdot}AsO_3H_2.$$

The iron solution (0·07 g. in 200 ml.) in 0·3–0·4*N*-mineral acid is treated at 80° with 0·75 g. of the reagent in 100 ml. of water. After

digesting for half an hour, the cold precipitate is collected, washed with 0·02*N*-hydrochloric acid, and ignited to Fe_2O_3. The precipitation permits a separation from Cu, Cd, Ni, Mn, Zn, Co, Al, Cr (reprecipitation necessary), Mg, Cu, V and Be (Craig and Chandlee, J. Amer. Chem. Soc. 1934, 56, 1278).

Cobalt.—Unlike nickel, cobalt is not satisfactorily separated from aluminium and iron by precipitation of the latter with ammonia and ammonium chloride although the basic acetate or succinate method is successful. Shaking a cobalt solution with an emulsion of zinc oxide *serves to remove a number of elements such as* $Fe^{\cdots}$, W (if fully oxidised), V, Cr, U, Zr, Ti, Al, P, As, Sn, and most of any Cu, Mo and Si (Evans, Analyst, 1925, 50, 389; Agnew, *ibid.* 1928, 53, 32; Hoffman, Bur. Stand. J. Res. 1931, 7, 883).

Nickel may be separated by means of dimethyl glyoxime or the cobalt may be precipitated with sodium hydroxide and hydrogen peroxide Nickel and manganese may also be removed by converting cobalt into potassium cobaltinitrite. For this purpose the solution should be free from metals of the first two analytical groups, from oxidising agents and ammonium salts, and should be concentrated 2–3 g. of potassium nitrite, dissolved in the least amount of 10% (by volume) acetic acid, is added to the faintly acid solution, and the mixture left for 24 hours with occasional stirring The filtered precipitate is washed with 5% potassium nitrite solution acidified with a few drops of acetic acid For purposes of estimation the cobaltinitrite must be dissolved in hydrochloric acid and potassium chromate or in nitric sulphuric acid and determined by one of the methods given below.

Methods of Estimation.—In general, electrolytic or volumetric methods are somewhat more accurate than most gravimetric procedures. Ignition to the oxide "Co_3O_4" provides a product of uncertain composition, while weighing as the sulphate is condemned by some workers It is probable, however, that with small quantities and a regulated ignition temperature below 550° the latter method is reasonably accurate

(*a*) *As* $CoSO_4$ *with Previous Precipitation as Sulphide*.—Colourless ammonium sulphide is added to the boiling ammoniacal solution and *the precipitate allowed to settle on a steam bath.* After filtering it is washed with cold 2% aqueous ammonium chloride containing a little of the reagent and then dried carefully in a platinum crucible. The paper is charred at a low temperature and after the carbon is burnt off the residue is converted to nitrate. Excess of nitric acid is removed and sulphuric acid then added; *after evaporating carefully* to dryness the sulphate is heated to 500°. It is allowed to cool, moistened with a little water, and reheated to drive out any occluded sulphuric acid.

(*b*) *With* 1-*Nitro-β-naphthol.*—The solution, containing 1–30 mg. of cobalt in 10–20 ml., is treated with 10 drops of 30% hydrogen peroxide and enough sodium hydroxide to precipitate $Co(OH)_3$. The precipitate is redissolved in 10 ml. of acetic acid, the solution diluted to 150 ml. with hot water and precipitated with about 1½ times the requisite amount of a 1% solution of the reagent in 50% acetic acid. The mixture is boiled, allowed to settle, and filtered on to a filter crucible. The precipitate is washed three times with 30% acetic acid and then with hot water. It is dried at 130° to constant weight and weighed as $(C_{10}H_6O\,NO_2)_3Co$, which contains 9 463% Co (Mayr, Z. anal. Chem. 1934, 98, 402).

α-Nitroso-β-naphthol may be used instead of the above reagent, the details being otherwise the same. The composition of the dried precipitate is $(C_{10}H_6O_2N)_3Co,2H_2O$ (Feigl and Mayr, Z. anal. Chem 1932, 90, 15). Nickel, zinc, chromium and aluminium do not interfere with these determinations.

Nickel.—No difficulty is experienced in separating this metal by usual methods from all but the members of its own analytical group.

Zinc may be removed by precipitation as ZnS in dilute sulphuric or formic acid solution (*q v*), manganese by deposition as the dioxide and cobalt by precipitating nickel with a dioxime

The use of dimethylglyoxime, $Me_2C_2(NOH)_2$, permits the estimation of nickel in the presence of many elements; more recently α furildioxime has been suggested as a substitute which possesses two advantages over the earlier reagent, namely, a greater solubility in water and a lower nickel content in the precipitate (11·81%) (Soule, J. Amer. Chem. Soc. 1925, 47, 981)

Estimation of Nickel.—*With Dimethyl glyoxime.* For this determination it is advisable to remove the hydrogen sulphide group, silicon, and tungsten, while iron must be oxidised to the tervalent state. Excessive amounts of ammonia, cobalt, or copper retard precipitation.

The nickel solution containing about 0 03 g of metal in 150–200 ml, and tartaric acid if group III elements are present, is boiled and ammonia added. If a precipitate occurs more tartaric acid is added followed by ammonia, this procedure being repeated until no precipitate is formed. *The solution is now made slightly acid* with hydrochloric acid, heated to 70°–80°, and treated with a slight excess of 1% alcoholic or ammoniacal dimethylglyoxime (about 15 ml. for 0 03 g). There is now added dilute ammonia drop by drop until precipitation takes place and then a slight excess. After one hour in a warm place, the precipitate is collected on a *filter crucible, washed with cold water, and dried* at 120°. It is weighed as $Ni(C_8H_{14}O_4N_4)$ which contains 20 31% Ni.

The ammoniacal solution of the reagent is made up in 11–12*N*-ammonia.

When much cobalt, zinc or manganese is present it is preferable to make the precipitation in a solution containing acetic acid and sodium acetate. If copper alone is the *contaminant it* need not be removed provided an excess of sodium hyposulphite is present.

Nickel may also be estimated by precipitation as $[NiPy_4](CNS)_2$ and ignition to the oxide. The complex pyridine thiocyanate is obtained when ammonium thiocyanate is added to a nickel solution containing pyridine. The wash liquor is a dilute solution of pyridine in water (Spacu and Ripan, J C.S. 1923, 124, ii, 585).

The Platinum Metals.—Minerals or alloys containing the platinum metals may be brought into solution in one of three ways:

(*a*) By prolonged attack with aqua regia which is eminently suitable for platinum alloys but not effective if much iridium, rhodium or ruthenium is present. Moreover, any osmium will be lost unless precautions are taken to collect it in some absorbing medium.

(*b*) By fusion with sodium hydroxide and peroxide or barium peroxide and nitrate; it is sometimes advisable to give a preliminary fusion with zinc chloride.

(*c*) *By heating with excess of sodium chloride* in a current of chlorine, although care must be taken to absorb any volatile products.

The platinum metals belong to the second analytical group and may thus be separated from all elements of succeeding groups by precipitation with hydrogen sulphide which is effected in almost boiling acid solutions and with a rapid stream of the gas; even so, complete deposition is slow, especially in the case of ruthenium. It has been recommended to accelerate the formation of sulphide by employing the gas under pressure.

Many elements may be removed by precipitating the noble metals by means of reducing agents such as zinc or magnesium or formic acid. Any of the baser metals also thrown down are dissolved either in nitric or hydrochloric acid. Using hydrogen under pressure, Ipatiev and Tronev (Compt. rend. Acad. Sci. U.R.S.S. 1935, 2, 29) have evolved schemes for separating the platinum metals in their binary mixtures.

The tendency for most of this group to form relatively insoluble double compounds with alkali chlorides has long been used as a method of separation, but it is difficult to render it quantitative without contaminating the precipitate. Rhodium is not precipitated by this method, palladium only in the presence of a moderately strong hydrochloric acid solution to prevent hydrolysis. Osmium and ruthenium may be separated from most other elements by distillation of their volatile tetroxides.

Quadrivalent compounds of the platinum group are easily hydrolysed to give the hydrated dioxides and this hydrolysis may be controlled so as to provide methods of separation. On this is based a recent method by Gilchrist and Wichers (J. Amer. Chem. Soc. 1935, 57, 2565) for the estimation of these metals in their mixtures, which is described below.

Separation and Estimation of the Platinum Group.—(1) *Estimation of Osmium.* The osmium is distilled from a dilute nitric acid solution in an all-glass apparatus consisting of distilling flask, fitted with thistle funnel and inlet and exit tube, the latter being joined to a train of absorption flasks. The tetroxide is absorbed in diluted hydrochloric acid (1 : 1) saturated with sulphur dioxide. The solution of the metals (100 ml.) is placed in the flask, 40 ml. of nitric acid added (1 : 1), and the liquid slowly distilled in a feeble current of air for one hour unless the osmium is present as chloro-osmate, in which case 7–8 hours is necessary. In the latter case it is quicker to distil from concentrated sulphuric acid. The absorbing medium is evaporated on a steam bath in an unetched beaker, as far as possible the residue digested with 10 ml. of hydrochloric acid for 15 minutes and again evaporated. This operation is repeated three times to ensure the destruction of any sulphite compounds and the final residue dissolved in 150 ml. of water. The solution is boiled and a filtered 10% solution of sodium bicarbonate added until a precipitate of the hydrated dioxide, OsO_2,xH_2O, appears and suddenly coagulates; bicarbonate is now carefully added until the solution is faintly blue to bromophenol blue. After further boiling for 5 minutes the liquor is filtered through a Munroe crucible, the precipitate washed with hot 1% ammonium chloride and then covered with solid ammonium chloride moistened with a few drops of the liquor which is sucked through. The crucible is fitted with its cap and with a quartz Rose lid. A Rose tube with a small flame of hydrogen burning from its end is inserted into the crucible; if the flame is extinguished it is relighted by bringing up a Bunsen flame for a moment. In this way sufficient heat is generated to dehydrate the osmium compound without risk of deflagration. After a few minutes the crucible is heated to expel ammonium chloride and then ignited strongly for 10 minutes. The burner is removed, the hydrogen flame extinguished, and the crucible allowed to cool in a current of hydrogen. When cold, the hydrogen is replaced by carbon dioxide and the product is weighed as metallic osmium.

(2) *Ruthenium.*—The residue in the flask after the removal of osmium is evaporated to dryness, 5–10 ml. of hydrochloric acid added and also evaporated. This is repeated until all the nitric acid has been destroyed. The residue, dissolved in 20–30 ml. of water, is treated with 10 ml. of sulphuric acid and heated to fumes of the acid. The solution, together with any platinum which may have separated, is returned to the flask and diluted to 100 ml. with water and 100 ml. of 10% aqueous sodium bromate added. It is now distilled for 1–1½ hours in a gentle current of air, the ruthenium tetroxide being absorbed in sulphurous-hydrochloric acid mixture as with osmium. A further 25 ml. of bromate is added and distillation continued for one hour. The combined absorbing solutions are evaporated to a moist residue on the steam bath, digested for half an hour with 10 ml. of hydrochloric acid, 50 ml. of water added, and the liquor boiled until all the ruthenium is dissolved. Traces of silica are filtered off and washed with dilute hydrochloric acid (1 : 99), the filtrate being diluted to 200 ml. with water. Precipitation with sodium bicarbonate is carried out as for osmium except that neutralisation is indicated by the appearance of the blue colour of bromocresol purple.

The precipitate is filtered on to paper, that remaining on the glass rod or the walls of the beaker being removed with filter paper, washed with hot 1% ammonium sulphate and then with cold 2½% solution of the same reagent. The paper and precipitate are dried in a porcelain crucible, charred carefully, ignited to remove carbon, and then heated in hydrogen as for osmium, being finally weighed as ruthenium.

Separation of Platinum from Palladium, Rhodium, and Iridium.—The residual solution after the removal of ruthenium is cautiously treated with hydrochloric acid to destroy excess of bromate and then evaporated with this acid on a steam bath. Any stain of iridium dioxide on the flask is removed with aqua regia and this likewise evaporated with hydrochloric acid and added to the main portion. The evaporated solution is diluted to 200 ml., boiled, and 20 ml. of 10% sodium bromate added, followed by 10% sodium bicarbonate until a slight permanent precipitate shows in the dark green liquid. Bicarbonate is now carefully added until bromocresol purple turns from yellow to blue, the test being made by taking up a drop of the solution on a rod, carefully running down a little indicator on to the drop, and noting the colour. More bromate is added (10 ml.), the mixture boiled, and bicarbonate added until a faint pink colour is developed with cresol red. A further 10 ml. of bromate is added and the liquor boiled for 15 minutes.

The precipitate of hydrated oxides of palladium, rhodium and iridium is filtered on to a porcelain filtering crucible, washed with hot 1% aqueous sodium chloride (p_H 6–7), and the crucible then placed in the beaker in which precipitation was carried out. The oxides are dissolved by warming with 10–20 ml. of hydrochloric acid, the crucible washed with water and transferred to another beaker where it is treated with a further 5 ml of the acid. This solution is added to the first portion and the operation repeated once more. The combined solution is then evaporated to dryness after the addition of 2 g. of sodium chloride. The residue is treated with 2 ml of hydrochloric acid, diluted to 300 ml. with water, and the precipitation repeated to ensure the removal of all the platinum.

Estimation of Platinum.—The two filtrates from the above precipitations are carefully treated with 20 ml. of hydrochloric acid, partially concentrated, combined, and taken to dryness. The residue is again evaporated with acid to destroy the last traces of bromate and the remainder is dissolved in water and filtered. The paper is washed with dilute hydrochloric acid (1 : 99), the filtrate diluted to some 400 ml and adjusted so that each 100 ml. contains 5 ml. of the mineral acid. Hydrogen sulphide is now rapidly passed into the heated solution and the process continued until all the platinum is precipitated and the solution has cooled somewhat. The sulphide is collected, washed with the diluted hydrochloric acid (1 : 99), and ignited in a porcelain crucible. The metallic bead is washed with hydrochloric acid, then with hot water, and again ignited. For the highest accuracy the metal is taken up in aqua regia, nitroso compounds removed, and the platinum precipitated with formic acid and sodium acetate. It is washed with hot 1% ammonium chloride and ignited.

Palladium.—The mixture of hydrated dioxides of palladium, rhodium and iridium is dissolved in hydrochloric acid as before, the solution after filtration being diluted to 400 ml. Sufficient of a 1% solution of dimethylglyoxime in 95% alcohol is added to precipitate the palladium and provide a 10% excess. After one hour the precipitate is collected on a filter crucible, washed with 1% hydrochloric acid and hot water, and dried at 110°. It is weighed as the glyoxime. $Pd(C_4H_7O_2N_2)_2$ contains 31 67% Pd.

Alternatively, the precipitate is collected on paper and ignited to the metal, first in hydrogen and then in carbon dioxide.

Rhodium.—The filtrate from the preceding operation is evaporated with sulphuric and nitric acids to destroy organic matter and then with water to remove nitrogen compounds and the resulting sulphuric acid solution removed to an unetched beaker and diluted to 200 ml. To the boiling solution is added titanous chloride (20% solution) until the supernatant liquor is slightly purple. After boiling for 2 minutes the metallic rhodium is filtered, washed with dilute sulphuric acid (2·5 . 97·5), and the paper and precipitate transferred to a conical flask. Sulphuric acid (10 ml) is added and the paper charred by gentle heating, after which 5 ml. of nitric acid are added. After digesting for a short time on a hot plate the flask is further heated over a free flame with constant shaking. The precipitate dissolves, organic matter is destroyed, and nitroso compounds are eliminated. Any silica is removed and the precipitation of rhodium repeated as above. The metallic rhodium is again dissolved as before, the final acid solution diluted with 20 ml of water and 10 ml. of hydrochloric acid The solution is boiled for 15 minutes during which time the colour becomes rose-red, filtered, and the paper washed with dilute hydrochloric acid (1 · 99). After dilution to 400 ml. the rhodium is precipitated as sulphide from a boiling solution which is finally allowed to cool somewhat with the gas still passing. The collected precipitate is washed successively with dilute sulphuric and hydrochloric acid wash liquors, ignited carefully in air in a porcelain crucible and then in hydrogen. After cooling in hydrogen the metallic rhodium is weighed.

Iridium.—The iridium may be determined by difference or directly after removal of titanium with cupferron In the latter case, the combined filtrates from the foregoing precipitation of rhodium are diluted to 800 ml., cooled in ice, and treated with cold aqueous 6% cupferron in slight excess. The precipitate, after washing with cold dilute sulphuric acid (2 5 · 97·5) is decomposed with nitric acid, fumed with sulphuric acid to destroy first organic matter and then nitroso compounds, diluted to 800 ml. and the precipitation of the titanium repeated.

The united filtrates are evaporated to about 10 ml. with, if necessary, the addition of nitric acid to destroy organic matter, and filtered after dilution. The filtrate is made up to 200 ml. with water and treated with sodium bicarbonate, as described under ruthenium, to the end point of bromocresol purple. After addition of 20 ml of 10% bromate and boiling for 25 minutes, the precipitate is collected, washed with 1% ammonium chloride, and dried in a porcelain crucible. It is moistened with a little saturated ammonium chloride, charred carefully in air

until carbon is oxidised, and then ignited in hydrogen. The iridium is leached with dilute acid and then washed with hot water and again ignited.

ULTIMATE ANALYSIS OF CARBON COMPOUNDS.

Most carbon compounds usually contain carbon, hydrogen and oxygen, while, in addition, there may occur nitrogen, halogens, sulphur, phosphorus, arsenic, antimony, silicon, or other elements. Therefore, before analysing an unknown organic substance it is necessary to carry out a qualitative examination.

QUALITATIVE TESTS.

Carbon.—Compounds containing carbon usually char when heated either alone or with strong sulphuric acid, while on heating with recently ignited copper oxide they evolve carbon dioxide.

Hydrogen.—Any water existing as such is first removed by heating the substance below its decomposition point and the dehydrated material is then heated with dry copper oxide. Any hydrogen present is oxidised to water which may be condensed and identified.

Nitrogen.—A limited number of nitrogenous compounds evolve ammonia when heated with soda lime, while others may give off oxides of nitrogen, with or without explosion when heated alone.

The element is generally detected by means of Lassaigne's or the Prussian blue test, which consists in heating the substance with a pellet of sodium or potassium in a small ignition tube. If the substance tends to be explosive then sodium carbonate may also be added. Generally the material is dropped on to the molten metal and heating continued for a minute or two. The hot tube is plunged into a little water contained in a beaker and, when the reaction has subsided, the glass is powdered and the solution filtered. To some of the filtrate is added ferrous sulphate solution, the mixture boiled, two drops of ferric chloride added followed by hydrochloric acid until the solution is acid. If the original material contained nitrogen then a blue precipitate should result. Sometimes only a greenish-blue solution is obtained, but if Prussian blue has been formed then this may be detected by filtration, when blue spots will appear on the paper.

The test fails with substances which readily evolve their nitrogen, such as diazo compounds, and also with stable pyrrole compounds which distil unchanged. It is stated that all classes of nitrogen compounds are decomposed by heating with a mixture of potassium carbonate and magnesium powder, but with this mixture it is necessary to exclude atmospheric nitrogen. This is most readily done by adding a little ether so that its vapour may displace the air and then stopping up the ignition tube with a wad of cotton wool (Baker and Barkenbus, Ind. Eng. Chem. [Anal]. 1937, 9, 135).

Halogens.—A rapid indication is obtained by heating the substance with a little copper oxide in a Bunsen flame, when the presence of halogens imparts a green colour to the flame. The method is not reliable but a confirmatory test can be made on a portion of the filtrate in the Lassaigne test. This solution is acidified with nitric or sulphuric acid, boiled to expel any cyanide or sulphide, and silver nitrate then added. Halogen may also be detected by igniting the substance with soda lime (free from chlorine) and testing the aqueous extract; in this case no cyanide can be formed.

Sulphur and Phosphorus.—The former element is usually detected in the filtrate from the sodium fusion by adding sodium nitroprusside; a purple-violet colour denotes the presence of sulphur. Alternatively the substance is fused with sodium peroxide and carbonate and the aqueous extract tested for sulphate. The extract also serves for the detection of *phosphate* and of *arsenate* and *antimonate*.

QUANTITATIVE DETERMINATIONS.

Carbon and Hydrogen in the Absence of Nitrogen, Halogens, etc.—The usual method consists in burning a known weight of material in a current of air or oxygen assisted by copper oxide. The carbon dioxide and water so produced are absorbed respectively by caustic potash or soda lime and calcium chloride or sulphuric acid.

The apparatus required comprises a combustion tube in which the substance is heated, a furnace as the source of heat, absorption tubes or bulbs, and a gas-purifying train.

The furnace consists essentially of a stand supporting a metal or fireclay trough in which the combustion tube rests, the latter being isolated from the trough by a layer of asbestos paper. The combustion tube is heated either electrically or by means of gas burners, each burner being fitted with its own tap to regulate the supply of gas to it. In the latter case also a system of fireclay tiles covers the trough, thus promoting even heating of the tube and minimising losses due to radiation. The tiles may be removed or opened so that the combustion tube may be rapidly cooled at one or more points. Electrically heated furnaces are generally made up in three sections, each of these consisting of a quartz tube on which the heating element is wound. This is surrounded by insulating material and the tube and insulation are enclosed in a sheet iron cylinder. The quartz tubes of the sections carry the metal trough, the ends of which can be fixed to the stand while by means of runners and a track the various sections may be moved to and fro, thus heating or exposing any portion of the combustion tube at will.

The combustion tube of hard glass has an internal diameter of about 12 mm., and is of such a length that it projects at least 5 cm. beyond each end of the furnace; its ends should be rounded off and slightly opened. After cleaning and drying the tube is filled in the following manner. A plug or spiral of copper about 2 cm. long is made by tightly winding copper gauze around a piece of stout copper wire the ends of which are turned into loops. This should fit the tube moderately tightly and is pushed in through one end for a distance of 20 cm. Through the other end is poured

coarse, freshly ignited copper oxide until a layer some 45 cm. long is built up, after which a second gauze plug is added. A third spiral about 10–15 cm. long and which has been superficially oxidised by heating in a large blow pipe flame is now inserted so that a space of 10 cm. is left between it and the previous plug; this space is reserved for the boat carrying the substance to be analysed. This end of the tube is now closed with a one-hole rubber bung carrying a glass tube of some 1–2 mm. bore and which is connected to the train for drying the air or oxygen. The opposite end is

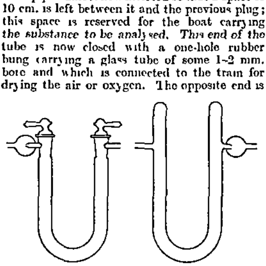


FIG. 1.

likewise fitted with a rubber stopper perforated to carry the first absorption tube.

The boat mentioned above is usually of porcelain or platinum and is about 7 cm. long, 8 mm. deep, and of such a width that it slides easily into the tube.

Water produced during the combustion is absorbed by means of calcium chloride contained in one of the forms of U tube illustrated in Fig. 1. This absorbent must be treated before use with a current of carbon dioxide in order to convert any oxide to carbonate; excess of the gas is then displaced by air or oxygen. Most of the water is condensed in the bulb of the side tube and can be removed after

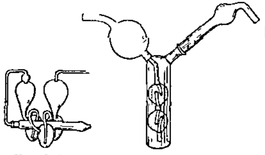


FIG. 2 (1). FIG. 2 (2).

each analysis, thus prolonging the life of the filling. Instead of calcium chloride there may be used small pieces of pumice or glass beads moistened with sulphuric acid, but only a minimum of acid should be used since it dissolves an appreciable quantity of carbon dioxide.

Caustic potash or soda lime is the usual absorbent for the carbon dioxide produced. The former reagent is used as a 50% solution contained in "potash bulbs," the most popular forms of which are the Geissler (Fig. 2 (1) and Bender (Fig. 2 (2)) patterns. In both cases the bulbs carry a small exit tube filled with granular calcium chloride or with soda lime and calcium chloride.

In the case of soda lime it is usual nowadays to employ one of the proprietary brands of soda lime asbestos such as *Sofnolite*, *Askarite*, or *Natronasbest*. These are impregnated with an indicator, the colour change of which serves to show both the rate of absorption and the amount of absorbent consumed. The soda lime is contained in a U-tube and above it on the exit side must be placed a few pieces of calcium chloride to absorb the water vapour formed in the reaction. Better still is it to employ two tubes, one filled entirely with soda lime and a second containing this reagent in the inlet limb and calcium chloride in the exit limb of the U tube.

Bulbs and tubes are protected when not in use by means of plugs made from short lengths of rubber tubing closed at one end with a piece of glass rod. These are removed for the purpose of weighing.

The oxygen or air used in the combustion is purified by passage through caustic potash solution and then through concentrated sulphuric acid. It is further dried using the same desiccating agent which is to be employed on the absorption side. The oxygen is most conveniently obtained from a cylinder of compressed gas and is drawn off through a reducing valve. Where such a source is not available it may be generated by adding a solution of 25 g. of potassium permanganate in 500 c.c. water and 50 c.c. of sulphuric acid to 500 c.c. of hydrogen peroxide (10 vol.) contained in a litre flask. Air should not be obtained from inside the laboratory but from an outside source, as laboratory air is often charged with organic material.

The purified and dried gas travels to the combustion tube through a small bubbler containing a little sulphuric acid and which indicates the rate of supply of the gas.

Operating the Combustion.—The tube is inserted into the furnace, connected to the drying train, and slowly heated to dull redness while a current of oxygen is passed through, the free end of the tube being closed with a calcium chloride guard tube. After 30–45 minutes, or when a blank experiment has shown that moisture and organic matter have been removed, the back half of the tube, that is, extending from the gas inlet end to some 12–15 cm. beyond the space reserved for the boat, is allowed to cool by extinguishing the burners and removing the tiles. During this time the substance is weighed into the previously ignited boat and the absorption tubes are also weighed after wiping with a lintless cloth and removing the guard plugs. When the tube is cold, the boat is inserted by withdrawing the oxidised copper spiral, pushing the boat in with a stout copper wire until it is close to the small plug which keeps the coarse copper oxide in place, and then replacing the oxidised spiral. The absorption apparatus is connected to the other end, care being taken that bulbs and tubes are joined by glass to glass connections covered with thick

seamless rubber tubing. A slow current of oxygen or air (about one bubble per second) is passed and then the last two or three burners under the long copper spiral are lighted, and the temperature raised to dull redness. The burners under the unheated portion of the coarse copper oxide are also lighted, while the heating of the spiral is extended also. A single small flame is now started under the boat itself or, in the case of more volatile substances, the heating is commenced by covering this portion of the tube with a hot tile from the rear end and replacing it when it has cooled somewhat by another heated tile. In any case the rate of combustion must be slow and regular until the material is completely carbonised. At this stage the temperature of the boat is increased, while if air has been used previously a change over is made to oxygen and the rate of passing the gas increased slightly. Finally, the boat is raised to dull redness and a somewhat faster stream of oxygen used to expel all the carbon dioxide and moisture as well as to oxidise any copper oxide reduced during the process. Any water which has collected at the end of the tube near the absorption tubes is removed by bringing a hot tile over this part of the tube. Oxygen is then replaced by air while the rear end of the tube containing the boat is allowed to cool in preparation for the next analysis. The absorption apparatus is now disconnected, plugs are replaced on the side arms, and the tubes or bulbs weighed after standing for one hour. A certain saving of time may be effected when a series of analyses is being done by weighing the absorption tubes filled with oxygen instead of air and using oxygen only for the combustions.

Volatile liquids are weighed in small glass bulbs with a capillary neck. The substance is introduced by alternately heating the bulb and cooling it with the open end immersed in the liquid. When the liquid is very volatile the capillary may be sealed before weighing, and the top broken off just before introducing the bulb into the combustion tube. In all cases the bulb is placed in the boat with the capillary facing towards the copper oxide layer and combustion must be carefully carried out, preferably using air for the first part of the procedure. The heating of the bulb should be by radiation only until all the liquid has been distilled out. Difficulty is sometimes experienced by the diffusion of the vapour into the back of the tube, but this may be overcome by inserting behind the copper spiral a bulb of hard glass of such a diameter that it just slides into the tube. One end of this bulb may be drawn out into a hook for convenience of withdrawal.

A few substances burn with great difficulty and in such cases they may be mixed in the boat with fine copper oxide and the combustion made entirely in oxygen. Compounds containing alkali metals are intimately mixed with lead chromate in order to decompose any alkali carbonates which may be formed.

Carbon and Hydrogen in the Presence of Nitrogen, Halogens, etc.—Substances containing nitrogen will tend to produce nitrogen oxides which must be reduced to the elementary state to prevent their absorption by the caustic potash or soda lime. This is achieved by introducing a spiral of reduced copper gauze about 12–15 cm. long into the absorption side of the combustion tube. The plug is reduced before use by heating to redness and dropping into a tube containing 2–3 ml. of methyl alcohol. Any flame produced is quickly extinguished. A bung carrying a piece of glass tubing is inserted and the tube evacuated quickly on a water pump, the vacuum being maintained until the tube is cold. Alternatively, the tube may be rapidly filled with methylated spirit, allowed to stand until cold, and the spiral then removed, washed with ether, and dried in a vacuum desiccator. A silver spiral is also used (*v. infra*) for the elimination of nitrous fumes, since it decomposes these catalytically.

The combustion is carried out without any air or oxygen passing until the material has been decomposed. One of these gases is then slowly introduced and the burners under the reduced spiral extinguished to prevent its oxidation.

If halogens are present these will react with the copper oxide to produce copper halides, which being somewhat volatile may be carried into the absorption tubes. This difficulty may be overcome either by inserting a spiral of silver gauze or by replacing part of the copper oxide layer by lead chromate. If much halogen is present it may be necessary to employ both methods. The section of the tube containing lead chromate should not be allowed to get too hot or it may fuse and, adhering to the glass, it will crack the tube on cooling.

Lead chromate must also be used when the substance contains sulphur, arsenic, or antimony. In these cases the chromate may replace most of the copper oxide or a mixture of chromate and copper oxide (3 : 1) may be employed.

Instead of copper oxide or lead chromate other oxidising agents have been recommended for the combustion of carbon and hydrogen. Ter Meulen and Heslinga (Rec. trav. chim. 1922–1926) use manganese dioxide with or without lead peroxide depending on whether nitrogen or halogens are present or not. This filling has the advantage that it promotes oxidation at temperatures between 250° and 450°, but as it rapidly becomes spent the method is best adapted for semi-micro analyses.

The vapour of the organic material may also be oxidised by activated platinum or palladium in a current of oxygen, a procedure which has been extensively employed by Dennstedt and his collaborators (Z. angew. Chem. 1905, **18**, 1134; **19**, 517; Chem.-Ztg. 1905, **29**, 52; 1909, **33**, 769; Analyst, 1905, 135; Ber. 1908, **41**, 600; Baumert, Ber. 1907, **40**, 3475). The Dennstedt method has also the advantage that it is possible to estimate sulphur or halogens simultaneously with the carbon and hydrogen.

Nitrogen.—Nitrogen is estimated either in the elementary condition by collecting it and measuring its volume (method of Dumas) or by conversion into ammonia (method of Kjeldahl).

Dumas' Method.—In this process the substance is oxidised with copper oxide and the liberated nitrogen is driven by carbon dioxide into a

suitable measuring vessel. The combustion is carried out in a tube similar to that used for carbon and hydrogen determinations excepting that when the carbon dioxide is generated inside the tube one end of the latter is sealed. This method has the disadvantage that the entire filling must be removed after each analysis in order to replace the spent magnesite or sodium bicarbonate which provides the source of the carbon dioxide. It is therefore more expedient to have both ends of the combustion tube open and to generate the gas in an ordinary Kipp's generator by acting on marble with hydrochloric acid. It is essential that the carbon dioxide shall be free from air and to achieve this the marble must be specially treated. First etched with dilute hydrochloric acid, it is then boiled in water for one hour and allowed to cool under the water. When cold the marble is transferred to a vacuum desiccator, covered with calcium chloride solution (spent liquor from the generator neutralised with marble), and a vacuum maintained for half an hour, and then slowly released. The Kipp is now charged, but the hydrochloric acid used will also contain dissolved air which may be removed by dropping a piece of marble into the upper bulb of the generator and opening and closing the tap a few times so that the acid in this bulb is continually changed.

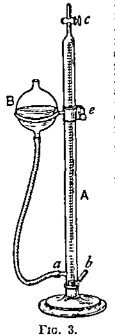


FIG. 3.

The combustion tube is filled by placing a tight copper plug about 20 cm from one end of the tube and then pouring in coarse copper oxide through a copper funnel inserted in the other end until a layer about 35–40 cm. long is obtained, after which a second plug is introduced. Some 3–4 cm of fine copper oxide is added, followed by an intimate mixture of the substance with more of this oxide. Enough of the material is weighed out to provide 15–25 ml of nitrogen and the mixing with recently ignited copper oxide is done in an agate or glass mortar free from cracks or scratch marks. The mixture is introduced into the tube through the copper funnel, and mortar and funnel are rinsed out three times with more copper oxide. Finally, a loosely fitting oxidised copper plug is inserted and the combustion tube removed to the furnace. The end of the tube containing the fine oxide is connected to the gas generator through a small bubbler containing water, while in the space left empty at the opposite end is inserted a spiral of reduced copper some 12–15 cm. long and a bung carrying a tube which makes connection to the nitrometer.

The latter consists of a burette A (Fig. 3), sealed at one end and fitted with a stop cock at the other. It is carried in a heavy base, while just above this a bent side tube is sealed in by means of which the nitrometer is joined to the combustion tube. On the opposite side of the burette and a little above the first side tube is inserted another connected by stout rubber tubing with a pear shaped reservoir carried in a ring clamped to the burette by means of which the height can be adjusted. Mercury is poured into the burette to seal up the lower side tube, the amount added being such that when the measuring tube is filled with potash solution none of this shall be able to force its way through the side arm into the combustion tube. The alkaline solution is made by dissolving caustic potash in 1–2 times its weight of water and, while still hot, adding about 0.2 g of powdered barium hydroxide and filtering through asbestos after stirring for a minute or two. The addition of this hydroxide may be omitted, but there is then a tendency for a scum to form on the potash while in the burette. The cold filtered solution is then introduced into the pear shaped reservoir.

The apparatus having been fitted together, carbon dioxide is passed through the combustion tube until all the air is expelled. During this time the stop-cock on the burette is open while the reservoir is at the bottom of the nitrometer. The burners under the reduced spiral and half of the adjacent coarse oxide layer are lighted and this section brought to dull redness. During this heating the gas entering the nitrometer is tested at intervals to ascertain whether all the air has been displaced. For this purpose the burette is filled with the potash solution, the stop cock closed, and the reservoir then lowered to the bottom again. If only carbon dioxide enters the nitrometer, then the bubbles will be completely absorbed and no more than traces of light foam will collect after 2–3 minutes. When this is the case the current of carbon dioxide is stopped and the heating of the tube gradually extended towards the fine oxide, while at the same time a few burners on the gas inlet side are lighted. When these parts are a dull red the heating of the fine oxide is commenced. Combustion of the substance must be at such a rate that there are never more than 2–3 bubbles rising in the burette at the same time. When all the burners are in use and the evolution of nitrogen has slackened carbon dioxide is again passed until the issuing gas is completely absorbed by the potash solution. The nitrometer is now detached from the combustion tube and the latter allowed to cool. The reservoir attached to the burette is now raised until the level of the liquid in it is the same as that in the burette and kept in this position for half an hour. The levels are again equalised and the volume of gas then read. The temperature recorded on a thermometer hung near the nitrometer is observed and the barometric pressure noted. The percentage of nitrogen is then given by the formula

$$P = \frac{100V\,(B-f)\,0.001251}{S\,(1+0.00366t)\,760},$$

where V is the observed volume, B the height of the barometer, f the vapour pressure of the potash solution at the temperature t°C., S the

weight of the substance in grams, and 0·001251 is the weight of 1 ml. of nitrogen at N.T.P.

Since the available data for evaluating f are very meagre it is usual to take instead half the value of the vapour pressure of water at the same temperature. Any error due to this may be avoided by transferring the nitrogen to a graduated eudiometer tube filled with water and again measuring the volume. This is most simply done by fitting to the nitrometer a narrow-mouthed bottle the bottom half of which has been removed (Fig. 4). This truncated bottle is filled with boiled out distilled water, any air in the narrow exit tube of the nitrometer is expelled with a fine wire and the eudiometer tube also filled with boiled out distilled water brought over it. By raising the reservoir and opening the stop-cock the nitrogen is transferred to the graduated tube. This is then removed, closing the bottom with the thumb, and transferred to a cylinder of water the temperature of which it is permitted to acquire, after which the levels of water in cylinder and tube are equalised and the volume read. The temperature of the water is also noted. Since tables are available which give the weight of nitrogen in 1 ml. of the moist gas at various temperatures and pressures the above formula may be considerably simplified by their use. The percentage of nitrogen is then given by:

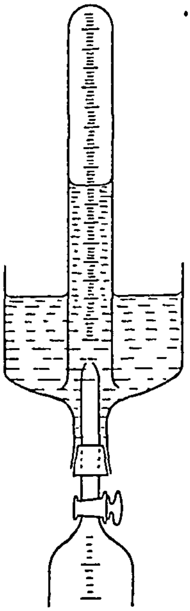


FIG. 4.

$$P=\frac{100\,V\,g}{S},$$

where g is the weight of nitrogen in 1 c.c. of moist N under the observed conditions of temperature and pressure. Usually g is recorded in milligrams, in which case S must also be expressed in milligrams.

The coarse copper oxide may be used for several estimations before it requires re-oxidising, but the fine oxide must be ignited before each analysis. The copper spiral is reduced with methyl alcohol as in the carbon and hydrogen determinations. Reduction with hydrogen should be avoided as the metal tends to occlude this gas.

Instead of using carbon dioxide to expel the nitrogen from the tube a Sprengel mercury pump may be employed to pump out the gas which is collected over mercury. It will, besides nitrogen, also contain carbon dioxide, and by noting the decrease in volume on absorbing the latter with potash a determination of the carbon may be obtained.

Kjeldahl's Method.—The substance is heated with concentrated sulphuric acid whereby carbon is oxidised to carbon dioxide and the nitrogen converted into ammonium sulphate. It is usual to add, in addition, potassium sulphate to raise the boiling-point of the acid and a catalytic agent such as mercuric oxide or metallic mercury in order to facilitate the oxidation of the carbonaceous matter. The solution, after dilution, is then rendered alkaline and the ammonia distilled into a known volume of standard acid representing an excess over that required to neutralise the base. This excess is then determined.

For carrying out the estimation about 0·3–0·4 g. of the material, depending on the amount of nitrogen it contains, is placed in a 150–200 ml. Kjeldahl flask together with 10 g. of powdered potassium sulphate and 0·5 g. of mercuric oxide (*not* made from nitrate) or 0·6 g. of mercury. Sulphuric acid (20–25 ml.) is added, the flask shaken to mix the contents and then clamped in an inclined position. It is now gently heated until any frothing has ceased, after which heating is increased until the acid boils gently. If a considerable amount of frothing takes place it may be minimised by adding a small piece of purified paraffin wax. Boiling is continued for at least 15 minutes after the liquid has become colourless or pale yellow. To prevent excessive loss of acid the neck of the flask may be closed with a loosely fitting bulb stopper or with a short stemmed funnel. The cooled liquid is then poured carefully into a 500 ml. flask containing about 100 ml. of water, the Kjeldahl flask rinsed out several times and these washings added also to the flask followed by 20–25 ml. of 0·5N-sodium metabisulphite or 0·2N-sodium sulphide

$$(Na_2S,9H_2O).$$

The sulphide material is added to decompose any mercury ammonium compounds which are not easily attacked by alkali. In addition, there may be added a little porous earthenware or granulated zinc to prevent bumping, although the mercury sulphide itself is generally sufficient to promote regular boiling. The flask is now fitted with a bung carrying a dropping funnel and a delivery tube which embodies some form of spray trap. This tube connects with a vertical condenser, the lower end of which dips just below the surface of the standard acid contained in a conical flask. Concentrated sodium hydroxide is run in through the dropping funnel until the liquid in the flask is strongly alkaline, the solution heated until it boils, and the ammonia distilled off with the steam. For complete expulsion of the ammonia it is necessary to collect about 100–150 ml. of distillate. The condenser is rinsed out with water and the excess of acid remaining in the conical flask is titrated.

This simple Kjeldahl estimation is unsuitable for nitrates, nitrites, nitro-, nitroso-, azo-, hydrazo-, and hydrazine compounds, and a special preliminary reduction process is necessary in such cases.

Nitrates and nitro-derivatives are usually treated by pouring quickly on to the weighed material about 20 ml. of a solution of salicylic acid (4–8 g.) in sulphuric acid (100 ml.), and heating gently until solution is complete and any reaction begins. After occasional shaking

for one hour there is added the reducing agent, which may be either 1–2 g. of pure zinc dust and one drop of mercury or 5 g. of sodium thiosulphate. When all the zinc has been consumed or immediately after addition in the case of the thiosulphate, the flask is gently heated until frothing has ceased, after which potassium sulphate and mercuric oxide or mercury are added and the estimation continued as before.

Azo- and hydrazo derivatives may also be treated by this method, but it is preferable to use stannous chloride as the reducing agent. For this purpose the substance (0·3–0 5 g) dissolved in 20 ml. of alcohol is boiled under a reflux condenser with 5–7 ml. of stannous chloride solution (40 g. in 100 ml. HCl) for 10 minutes after the solution is bleached (about 20 mins. in all). On cooling there is added an equal volume of water and 25–30 ml. of sulphuric acid. The liquor is gently heated to remove water and when any foaming has *ceased the determination is continued in the* usual way by introducing potassium sulphate and the mercury catalyst.

Hydrazines, semicarbazides, etc., may be reduced with zinc and sulphuric acid, finally using potassium persulphate in place of potassium sulphate or by heating under a reflux condenser with formaldehyde, zinc dust, and hydrochloric acid, adding a *little* stannous chloride towards the end to complete the reduction. In the latter case the subsequent procedure follows that given in the preceding method.

Numerous modifications of all the above estimations are constantly being introduced, and a recent summary of the literature is given by A. Friedrich (Mikrochem. 1933, 13, 91).

Instead of mercury as the catalyst there have been suggested copper sulphate, copper selenite, tellurium, selenium, titanium, molybdenum, and many other metals. Tellurium and selenium (also copper selenite) are stated to be very effective although the presence of selenium in too great concentration tends to cause a loss of nitrogen if heating is unduly prolonged; this results from the decomposition of ammonium selenite thus:

$$3(NH_4)_2SeO_3 = 9H_2O + 2NH_3 + 3Se + 2N_2$$

(Täufel, Thaler, and Starke, Angew. Chem. 1935, 48, 191; 1936, 49, 265; Osborne and Wilkie, J. Assoc. Off. Agric. Chem. 1935, 18, 604; Illarionov and Solovjeva, Z. anal. Chem. 1935, 100, 328; Schwoegler, Babler, and Hurd, J. Biol. Chem. 1936, 113, 749).

Estimation of Halogens.—*Carius Method.*—The substance to be analysed is oxidised in a sealed tube with fuming nitric acid and in the presence of silver nitrate; the resulting silver halide is weighed or, if a known weight of silver nitrate is taken, the excess of the latter may be determined volumetrically. The tubes used are of fairly hard glass some 15 mm. in diameter and with walls about 2 mm. thick; they are 50–60 cm. long and are sealed at one end.

Into the cleaned and dried tube are placed a slight excess of silver nitrate (about 0 5 g. is *usually sufficient) and 1·5–2 c.c. of nitric acid* (d=1·5), the latter being poured in through a long thistle funnel which is then carefully withdrawn so as to avoid wetting the sides of the tube. The substance to be analysed (about 0 2 g.) is now weighed into a narrow tube made from quill tubing and which is 7 cm. long and 0 8 cm. in diameter. This is inserted into the Carius tube by inclining the latter and gently sliding the weighed tube down the side. The combustion tube is next drawn out to a thick capillary and sealed, care being taken that during this process the nitric acid is not allowed to enter the small tube. When cold, the tube is wrapped in a few turns of paper and inserted into an iron or steel tube so that the whole of the capillary projects from this tube, which is then introduced into the furnace. The latter consists of a rectangular sheet iron box constructed to stand in an inclined position and containing 3 or 4 tubes into which the above-mentioned iron or steel tubes are placed. The furnace is heated by means of Bunsen burners, *while a tube inserted into its upper surface* serves as a thermometer pocket; it is usual to surround the furnace with a well protected enclosure (Fig. 5). Heating should be carried

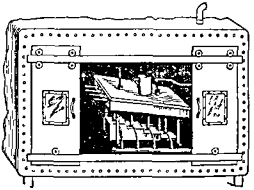


FIG. 5.

out in a slow and regular manner so that a temperature of 250°–300° is reached in 2½–3 hours, this temperature being then maintained for 3–4 hours. When cold the combustion tube is opened by gently warming the capillary to remove any condensed acid and then, strongly heating the extreme tip until a hole is blown at this point by the imprisoned and compressed gas. On no account should the tube be removed from the furnace until the pressure has been released in this way. The drawn out portion of the tube is now cut off, some distilled water added, and the contents transferred to a beaker. Combustion tube and weighing tube are rinsed several times with water until all the silver halide has been removed to the beaker. The liquid is then boiled for some half an hour in the case of silver chloride or bromide and for 2 hours when silver iodide is present, after which the precipitate is allowed to settle. It is filtered, washed, dried and weighed in the usual manner.

Volatile liquids may be weighed in a small thin-walled bulb tube which is sealed after introducing the substance and inserted into the Carius tube after weighing. When the latter *is sealed the small bulb is shattered* against the side walls of the tube.

Method of Piria and Schiff.—This procedure is a modification of Liebig's original method in which the substance was heated with lime in a combustion tube. In the present case two nickel crucibles are used, one of which when inverted may be inserted into the other, while instead of lime a mixture of lime and sodium carbonate (4 : 1) is used. A layer of this mixture is placed on the bottom of the smaller crucible followed by an intimate admixture of a weighed amount of the substance and the lime-carbonate. The crucible is now filled with lime and carbonate, placed in an inverted position in the larger crucible which is also filled with the mixture to just above the top of the inner crucible. After covering the outer crucible with a lid it is heated with a burner which is first directed around the sides of the crucible until the lime and carbonate between the crucibles are thoroughly hot. Heating is then continued underneath the crucible until decomposition of the substance is deemed to be complete. When cold, the contents of the crucibles are transferred to a beaker and the crucibles then washed out with about 200 c.c. of water. The lime is now carefully dissolved in dilute nitric acid, the beaker being cooled in ice during this process to prevent loss of halogen. If iodine is being estimated then sulphur dioxide solution must be added before the nitric acid in order to reduce calcium iodate. The halogen in the acidified solution is estimated in the usual manner.

Method of Stepanov.—Decomposition of the material is effected in this process by boiling with alcohol (20–40 c.c.) and adding a considerable excess of sodium at such a rate that a vigorous action is maintained:

$$XCl+2Na+C_2H_5{\cdot}OH = XH+NaCl+C_2H_5{\cdot}ONa$$

The amount of sodium required varies from about six times the weight of substance taken in the case of iodo- derivatives to twenty times when chlorine is being estimated. After addition of the sodium the solution is boiled for one hour, cooled somewhat, and diluted with 20–40 c.c. of water. Alcohol is removed and the halogen determined in the aqueous liquor by known means (*see* Bacon, J. Amer. Chem. Soc. 1909, 31, 49).

Method of Grote and Krekeler.—*See* below, under Sulphur.

Estimation of Sulphur.—*Method of Carius.*—Excepting for the omission of the silver nitrate this method is identical with that described above, although in certain cases it may be necessary to heat the tube to 300°–350° to ensure complete decomposition. The sulphuric acid produced is estimated in the usual manner with barium chloride after concentrating the solution with hydrochloric acid to remove excess of nitric acid. This concentration may be avoided if the barium chloride is run in drop by drop with good stirring to the hot and rather dilute sulphuric acid solution.

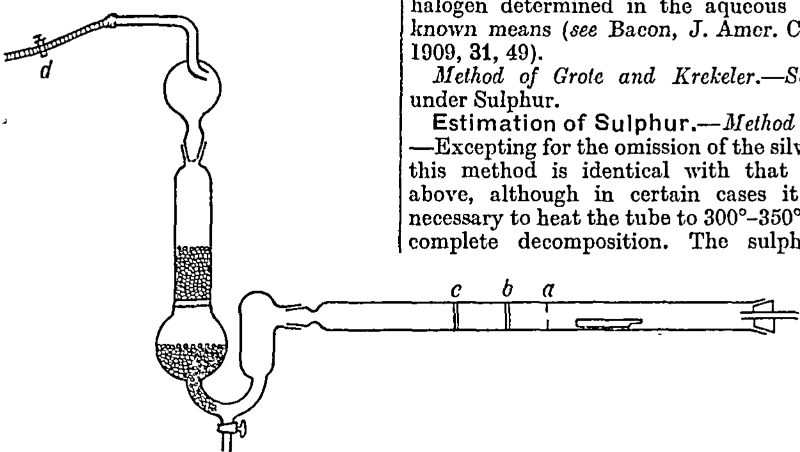


FIG. 6.

Method of Eschka.—*See* under Gravimetric Estimation of Sulphur p. 603.

Method of Grote and Krekeler (Angew. Chem. 1933, 46, 106).—This is a combustion method whereby it is possible to estimate sulphur in any substance which can be burned.

The apparatus (Fig. 6) consists of a quartz tube (50 cm. long and 17 mm. internal diameter) connected by a ground glass joint with an absorption vessel. Fused into the central portion of the tube are (*a*) a perforated plate of clear quartz, and (*b*) and (*c*) two quartz filter discs. The plate serves to mix the vapours of the substance with the air needed for the combustion and also to prevent any unvaporised liquid from reaching the first disc. Combustion should take place entirely at this disc, the second one merely being a safeguard in the event of incomplete oxidation at the first. A small asbestos-lined box movable on rails covers the portion of the tube carrying the discs and serves to concentrate the heat of the burner at this point.

The absorption vessel contains a thick, finely perforated glass filter plate, while glass beads are introduced above and below this plate. The absorbing liquid consists of 50 c.c. of 3% hydrogen peroxide half of which is contained above the filter disc and half below. Most of the SO_3 produced is absorbed in the lower half, the function of the filter disc being to coalesce the acid particles in the fine mist which is also produced and which tends to pass through any liquid.

The material to be analysed is weighed into a combustion boat which is then inserted into the tube until it is about 1–3 cm. from the perforated plate. The amount of substance to be taken varies from 100 mg. if the sulphur content exceeds 1% to 3–5 g. for proportionately lesser percentages. If the sulphur content is so

high that only a small amount of substance is required, then, for ease of combustion, it is advisable to add some sulphur-free material such as liquid paraffin.

To carry out the operation the filter discs are first heated until they glow. A current of air (three bubbles a second) is then drawn through the tube by means of a pump, this current being regulated by the screw-clip (*d*). The boat is now gently heated from the gas inlet side until the substance vaporises and a small blue flame appears at the first disc (*b*). The flow of air may now be increased and also, if necessary, the amount of heat supplied to the boat until a fairly large flame occurs at the disc. Combustion is complete in 6–10 minutes, after which the air supply is decreased and any liquid collected between the boat and the perforated plate is vaporised. That portion of the tube between the filter discs and the ground glass joint is strongly heated to remove any SO_3, and in a few minutes the receiver may be disconnected. The absorbing medium is sucked out through the cock at the bottom of the absorption vessel, which is then washed twice with water. The sulphuric acid in the resulting solution is determined in the usual manner.

By using an absorption liquid of 8 parts of crystallised sodium sulphite in 100 parts of 0·1*N*-sodium hydroxide the apparatus may be used to estimate halogens.

Estimation of Phosphorus.—*Method of Carius.*—This method as used for sulphur also serves for the determination of phosphorus in organic compounds. The resulting phosphoric acid is precipitated as magnesium ammonium phosphate, which is subsequently ignited to pyrophosphate, $Mg_2P_2O_7$.

Messinger's Method.—The organic material (0·3–0·4 g.) is placed in a flask fitted with a ground-in condenser through which is added the oxidising agent consisting of 4–5 g. of chromic acid and 10 ml. of sulphuric acid. The mixture is gently heated for one hour, after which a further 10 ml. of sulphuric acid are added and heating continued for another hour. The contents of the flask are washed into a beaker, heated on a steam bath, and the phosphate precipitated as phospho molybdate. The precipitate is collected, washed with a dilute solution of ammonium nitrate and nitric acid, and dissolved in ammonia. The phosphate is now precipitated with magnesia mixture, a few drops of citric acid solution being added to prevent any precipitation of chromium caught in the molybdate precipitate (Ber. 1888, **21**, 2916).

Other oxidising agents that may be used are nitric acid and potassium permanganate or nitric and sulphuric acids.

Estimation of Arsenic.—*Method of Little, Cahen, and Morgan* (J.C.S. 1909, **95**, 1477).—For details, *see* Volumetric Analysis (pp. 645, 653).

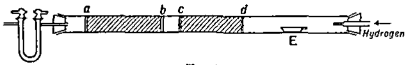


FIG. 7.

Estimation of Antimony.—Organic antimonials may either be decomposed by fusion with peroxide and carbonate or by heating with nitric and sulphuric acids. The antimony is estimated as sulphide as given under Gravimetric Analysis (*see also* Morgan and Davies, Proc. Roy. Soc. 1926, **110**, A, 530).

Estimation of Oxygen.—Although oxygen in organic compounds is usually estimated by difference various methods for determining the element have been put forward from time to time. It is only recently, however, that reliable methods have been elaborated, these being based largely on the work of H. Ter Meulen (Rec. trav. chim. 1922, **41**, 509; 1924, **43**, 899; 1934, **53**, 118). The procedure consists in distilling the material on to a red hot contact substance which decomposes it producing water and oxides of carbon, the latter being then hydrogenated to methane and water by means of hydrogen and a nickel catalyst. The water is absorbed in a weighed calcium chloride tube, while a small soda lime tube takes up any traces of carbon dioxide which may have escaped reduction. Several modifications have been suggested at various times, especially by Russell, Fulton and Marks (Ind. Eng. Chem. [Anal.], 1933, **5**, 384; 1934, **6**, 381; 1935, **7**, 102; 1936, **8**, 453).

The hydrogenation is carried out in a clear quartz tube 1 m. long, 1 cm. in diameter, and with 1 mm. walls, and where only carbon, hydrogen, and oxygen are present the apparatus shown in Fig. 7 is used. E is a small platinum or quartz boat carrying the material, while at *c–d* is inserted the contact material consisting either of pure asbestos, platinised asbestos, platinised quartz, or spirals of pure nickel wire, this being heated in a small Fletcher furnace or electrically. The catalyst is contained between *a* and *b* and consists of nickel supported on asbestos or quartz and preferably activated by 2–10% of thoria. It may be made by shaking up asbestos with nickel oxide (iron free) and thoria and then reducing with hydrogen after placing in the tube, or quartz grains may be soaked in nickel and thorium nitrates, ignited after drying and again reduced after filling into the tube. The catalyst is heated in some simple form of furnace to a temperature between 300°–400° although for the preliminary reduction of the nickel oxide a temperature of 400°–450° is advisable. This reduction of the oxide is often very slow, especially if the nickel contains iron, and even so it is advisable to run a blank estimation and to subtract its value from that obtained during the analysis. The hydrogen may be produced either electrolytically or from zinc and acid; it is purified through alkaline and acid permanganate as well as silver sulphate, while traces of oxygen are removed by passing over platinised asbestos. Any water produced is

absorbed by passage through a cooled calcium chloride tube.

To carry out the estimation the tube is first filled with CO_2 or air may be removed by evacuation and hydrogen is then led in. The contact material and catalyst are raised to red heat and 350° respectively, after which the boat is introduced without allowing air to enter the tube and the absorption train attached at the other end. The substance is now heated slowly and regularly until it has all been decomposed or distilled on to the cracking surface, after which the whole of the tube on the gas inlet side is strongly heated with either a Bunsen burner or, better, a blast flame. At the end of the hydrogenation the tubes are removed, dry CO_2-free air passed through them, and weighed. As much carbon collects in the quartz tube it is necessary to burn this out with air after three or four analyses.

When the substance contains nitrogen the hydrogenation will give rise to certain quantities of ammonia which would be absorbed by calcium chloride. Ter Meulen therefore uses an absorption tube which is in two parts, the first containing a known volume of standard sulphuric acid to absorb ammonia and the other calcium chloride. Ammonia and water are thus weighed while by titrating the excess of standard acid the weight of ammonia may be calculated. Obviously a simpler method would be to use an absorbent which does not take up ammonia, and consequently Russell and Marks have advocated pellets of sodium hydroxide, while Marks uses calcium sulphate.

Sulphur-bearing compounds form hydrogen sulphide, most of which is retained by the nickel in the tube, thus poisoning the catalyst. To ensure retention of all the sulphide Ter Meulen uses an additional filling of finely divided nickel heated to 150°, but if calcium sulphate is used to absorb water no such precaution need be taken.

Halogens are also mostly retained by the nickel though varying small amounts come through and must be absorbed in a manner similar to ammonia except that sulphuric acid is replaced by standard silver sulphate solution.

Proximate Analysis of Carbon Compounds.

Methods available for the separation of the constituents of any particular mixture of organic compounds will depend essentially on the nature of the mixture and must be found out by trial. A few of the more general methods usually employed are briefly described.

Fractional Distillation is used for the separation of liquids which possess boiling-points fairly considerably removed from each other.

Certain substances are volatile in steam and can thus be removed from others which do not exhibit this property. Where two compounds are to be separated both of which distil, then it is often possible to convert one of them into a non-volatile derivative. Thus volatile organic acids and bases may be separated by distilling either from solutions containing mineral acid which fixes the bases or from caustic alkaline solutions which render the acids non-volatile. Steam distillation can be carried out under reduced pressure, while in some cases it is necessary to use superheated steam.

Fractional Precipitation.—As in inorganic analysis, reagents may be found which precipitate some members of a mixture while other remain in solution. Also if the components resemble each other and are present in sufficient amounts, advantage may be taken of their differing order of precipitation by a known reagent added in successive small quantities. Thus, if a calcium salt be added to a mixture of neutral salts of oxalic, malonic, and succinic acids, calcium oxalate is precipitated first, the middle fractions will contain most of the malonate, while the end fractions give calcium succinate. Silver and lead salts are often advantageously used for separating such organic acids.

Fractional Crystallisation is used where substances differ in their solubilities in any given solvent. The solution when partially concentrated deposits crystals of the least soluble compound, while further concentrations yield mixtures differing in composition and in which are increasing proportions of the more soluble members. The various fractions or groups of fractions are submitted to the same procedure and a separation gradually effected.

Fractional Solution is perhaps the method most generally applicable, for the range of solvents available is so great that it is not difficult to find a menstruum which will dissolve one component of a mixture more readily than the others. Where substances differ widely in their solubilities in any one solvent the more soluble material may be leached out with successive small quantities of the liquid. The solvents most commonly used are given below together with their general properties.

Water dissolves many acids and their salts, also organic bases and salts; also serves for highly oxidised carbon compounds, such as carbohydrates, gums, alcohols, polyhydric phenols, etc., which are not readily soluble in alcohol or ether. Very many organic substances do not, however, dissolve in water, while it decomposes others such as acid chlorides, anhydrides, esters, etc.

Alcohol has considerable solvent properties and is useful for many classes of organic substances. Like water it reacts with certain halogen derivatives.

Ether dissolves a large variety of materials such as hydrocarbons, resins, fats and alkaloids. It is relatively inert and has the advantage of a low boiling-point, so that it can easily be removed by distillation.

Benzene and its homologues are useful solvents for oils, fats, waxes, terpenes, resins and rubber; they also serve for such substances as are decomposed by water.

Carbon disulphide, like ether, is easily volatile, but it possesses a far more limited application. It dissolves fats, essential oils, resins and rubber, but salts and hydroxylic compounds are generally insoluble in this medium.

Light Petroleum.—Generally obtainable in three fractions, boiling at 40°–60°, 60°–80°,

80°–100°; it has limited solvent properties, although it is much used for oils and fats.

Chloroform, Methylene Dichloride, and Carbon Tetrachloride dissolve many substances, especially oils, fats and alkaloids, and are, in addition, practically non inflammable. Other non-inflammable solvents are the chloro-derivatives of ethane and ethylene.

Some of the solvents which are also used, although less frequently, are acetone, ethyl acetate, amyl alcohol, pyridine and nitrobenzene.

The extraction of a substance from admixed solids by means of a volatile solvent is best carried out in a Soxhlet extractor. This consists of a wide tube E (Fig 8) closed at the bottom end and sealed to a narrower tube N which is fitted to a small flask either by means of a cork or a ground glass joint. Connection between the two tubes is effected by means of (*a*) a narrow tube *s* serving as a siphon, and (*b*) a wide tube *t* The latter tube carries the vapour of the solvent boiling in the flask to the top of the extractor which is connected with a reflux condenser. The condensed solvent drops

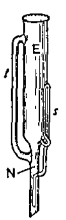


FIG. 8.

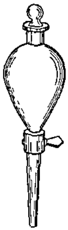


FIG. 9.

on to the material to be extracted and which is contained in a thimble made of filter paper inserted into E so that its upper end is above the level of the top of the siphon. The liquid percolates through the material, is filtered through the paper, and rising in the tube is siphoned off when it has reached the bend of the narrow tube *s*. The process continues automatically and the extracted substance gradually accumulates in the solvent in the flask. When extraction is complete the liquid is distilled and the residue recovered.

Where the required material is found in solution it may often be removed by agitating the liquid with a non miscible solvent. For this purpose a pear- or tube shaped separating funnel is employed (Fig. 9), one end of which is fitted with a stop-cock while the other is closed with a stopper. Liquid and solvent are thoroughly agitated in this apparatus and, after separating, the lower layer is run off through the stop-cock while the upper layer is poured through the top or drawn off through a glass tube by means of suction. The number of extractions necessary will depend on the relative solubilities of the material in the original solvent and extracting medium.

ESTIMATION OF RADICALS COMMONLY OCCURRING IN ORGANIC COMPOUNDS.

In an article such as this it is not possible to do more than indicate a few of the most general methods available for the estimation of some of the typical radicals found in organic compounds.

Hydroxyl.—Of two methods which are available the first depends on the formation of an acetyl derivative followed by the estimation of this group (*see* under ACETYL p. 625), while in the second there is determined the volume of methane produced on interaction with methyl magnesium iodide (Grignard's reagent):

$$R{\cdot}OH+CH_3MgI=R\,OMgI+CH_4$$

This method is really an estimation of active hydrogen and can therefore be used also for the estimation of sulphydryl (SH), imino- and amino- groups; it also follows that all reagents and apparatus must be scrupulously dried.

For the procedure the substance (0 1–0 25 g) is placed in a glass bottle (Fig. 10) together with 10–20 ml. of dry amyl ether, phenetole, or pyridine. Excess of Grignard's reagent in one of the above solvents is placed in a tube which is also inserted in the bottle and the latter then connected to the burette filled with dry mercury. The bottle is brought to constant temperature by immersing in a bath and the burette reading taken under atmospheric pressure. The contents of the tube and bottle are allowed to mix with thorough shaking and after all the methane has been evolved the temperature is again allowed to become constant and the new burette reading is taken (Hibbert and Sudborough, J C S. 1904, 85, 933; Zerewitinoff, Ber. 1907, 40, 2023).

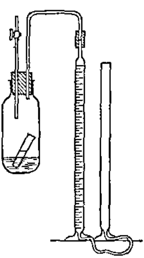


FIG. 10.

Methoxyl.—This important radical occurring in many natural organic compounds is usually determined by some modification of Zeisel's method, which consists in decomposing the material with hydriodic acid (free from sulphur compounds) or with a mixture of this acid and acetic anhydride. The methyl iodide formed is

absorbed in alcoholic silver nitrate and the precipitated silver iodide is weighed; each $-OCH_3$ is equivalent to 1 mol. of AgI.

The simplest modification is that due to Perkin (J.C.S. 1903, **83**, 1367) in which the substance (0·3–0·4 g.) and the hydriodic acid *d*1·7 (15 ml.) are placed in a 200 ml. distilling flask A (Fig. 11) having a long neck, the side arm being some 20 cm. above the top of the bulb. The flask is heated at 130°–140° in an oil-bath while carbon dioxide is passed through the apparatus. The methyl iodide is collected in two flasks B and containing respectively 20 and 15 ml. of aqueous alcoholic silver nitrate made by dissolving 2 g. of the salt in 5 ml. of water and adding 45 ml. of pure alcohol; one drop of nitric acid is also added to each flask. After heating the distilling flask for one hour the temperature of the bath is raised until the hydriodic acid boils gently but without distilling into the side arm. The operation is complete when on substituting for B the V-tube D containing a few ml. of the silver nitrate solution no turbidity is noticed after 15 minutes. The contents of the flasks are washed into a beaker containing 50 ml. of boiling water acidified with nitric acid and the silver iodide is collected after boiling for one to two hours.

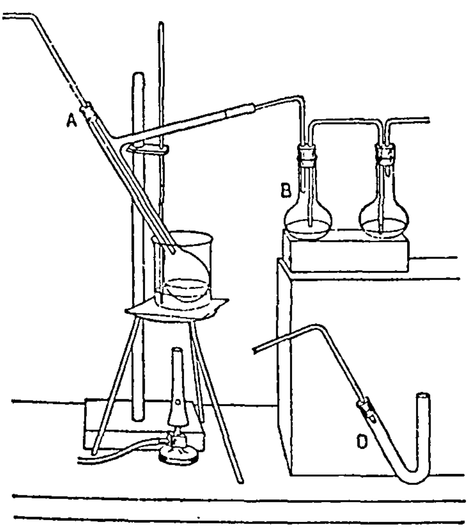


FIG. 11.

Hewitt and Jones (J.C.S. 1919, **115**, 193) absorb the methyl iodide in pyridine, thereby converting it into pyridine methiodide in which the iodine, being ionised, may be estimated by adding excess of standard silver nitrate solution and determining this excess by Volhard's method.

Methyl.—A modification of Zeisel's methods permits its use for the estimation of methyl groups attached to nitrogen. Here the substance is heated with hydriodic acid and dry ammonium iodide. To decompose the resulting quaternary ammonium salt it is usually necessary to distil off the acid and heat the residue to 300°–350°, the evolved methyl iodide being absorbed as indicated above. It is obvious that a vessel must be inserted to catch the hydriodic acid, while it is also necessary to provide a trap containing a mixture of cadmium sulphate (5%) and sodium thiosulphate (5%) to retain hydrogen sulphide, hydriodic acid, and iodine (Herzig and Meyer, Ber. 1894, **27**, 319; Monatsh. 1894, **15**, 613; 1895, **16**, 599; for the adaptation to micro-analysis, *see* Pregl-Roth, "Quantitative Micro-Analysis").

Acetyl.—This radical is determined by hydrolysis either in alkaline or acid media. In the former case the substance is boiled with a known volume of an aqueous or aqueous-alcoholic standard solution of alkali excess of which is then found by titration. A control experiment is necessary to determine the changes occurring in the standard alkali during the process. In the original method of acid hydrolysis due to Wenzel (Monatsh. 1893, **14**, 478; 1897, **18**, 659) the acetyl derivative is heated with dilute sulphuric acid (1 : 2) after which mono-sodium phosphate (NaH_2PO_4) is added, and the mixture concentrated under reduced pressure, the acetic acid which distils over being collected in excess of standard alkali. The phosphate serves to fix the sulphuric acid and prevent its decomposition with the liberation of sulphur dioxide. To prevent the possibility of sulphur dioxide being formed Sudborough and Thomas (J.C.S. 1905, **87**, 1752) have recommended the use of aromatic sulphonic acids as hydrolysing agents. The substance (0·2 g.) is treated with 100 ml. of a 10% benzene-sulphonic acid solution and steam passed through so that 400 ml. of distillate are obtained per hour, distillation being continued until the liquor passing over is neutral. The acetic acid is then titrated with standard barium hydroxide.

In a method due to A. G. Perkin (J.C.S. 1905, **87**, 107; 1907, **91**, 1230) hydrolysis is effected with sulphuric acid in the presence of alcohol whereby ethyl acetate is formed and removed by distillation into a known volume of standard alkali. The ester is hydrolysed and the excess of alkali then determined (*see also* Phillips, Ind. Eng. Chem. [Anal.], 1934, **6**, 321).

Carboxyl.—Provided that the molecular weight of the substance is known it is possible to estimate the number of carboxyl groups present either by the analysis of its neutral salts or by titration with a standard solution of a base.

For the former procedure the silver salts are the most suitable, as they are generally anhydrous as well as normal salts and, moreover, can, in most cases, be easily prepared by the interaction of a neutral salt of the acid with silver nitrate. Direct ignition of these salts leaves a residue of silver which may be weighed, but in some cases they decompose too violently for ignition and must then be heated with aqua regia, which destroys the organic matter and converts the silver into chloride which is weighed as such. A few also are sensitive to light and must be protected from sunlight during preparation. Certain aromatic hydroxycarboxylic acids (*e.g.* 3:5-dinitro-*p*-hydroxybenzoic acid) take up two atoms of silver, one of them replacing the phenolic hydrogen.

Other salts which may be used are those of lead, copper (often suitable for amino-acids), calcium and barium, the last two being useful for dibasic acids with which they often form insoluble salts

Titration methods usually employ barium hydroxide as the base although standard aqueous or aqueous alcoholic solutions of sodium or potassium hydroxide may also be used. The acid may be dissolved either in water or neutral alcohol or ether, while the most suitable indicator is phenolphthalein.

The weaker fatty acids may be conveniently estimated by the following indirect method. 1 g. of the substance is dissolved in alcoholic potash (the alcohol being at least 93%), and excess alkali is precipitated as carbonate or bicarbonate by saturating with carbon dioxide. After filtering the precipitate and washing with alcohol the filtrate is concentrated to remove alcohol and the residue containing the potassium salt of the acid is heated with 10% aqueous ammonium chloride, the evolved ammonia being collected and estimated as in Kjeldahl's method (p. 619).

Carbonyl.—The carbonyl group in all aldehydes and some ketones (not mixed ketones or ketonic acids) may be detected by the green fluorescence produced when an aqueous or alcoholic solution is heated with a 1% solution of *m*-phenylenediamine hydrochloride. The radical is best identified, however, by its ability to form hydrazones with phenyl hydrazine or its substitution products (especially 2 4-dinitrophenylhydrazine) and semi carbazones with semicarbazide. These derivatives are usually well defined and crystalline.

If in the production of a phenylhydrazone from a known weight of carbonyl compound and phenylhydrazine the excess of the latter is determined, then it is possible to estimate the carbonyl group. The uncondensed phenyl-

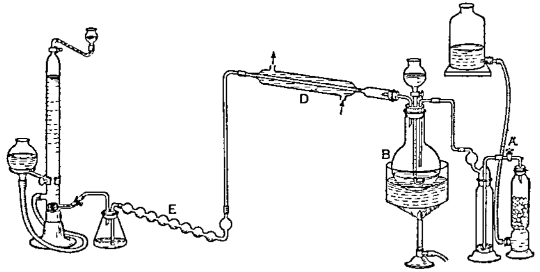


FIG. 12.

hydrazine is decomposed by Fehling's solution according to the following equation and the nitrogen liberated is measured.

$$C_6H_5{\cdot}NH\,NH_2+2CuO = C_6H_6+H_2O+N_2+Cu_2O$$

Fehling's solution is a two-solution reagent consisting of (*a*) 69 28 g. $CuSO_4,5H_2O$ per litre and (*b*) 350 g. of Rochelle salt and 120 g. of NaOH per litre. Equal volumes of (*a*) and (*b*) are taken and mixed before use.

For the estimation the apparatus in Fig. 12 is used and consists of a flask B connected to a carbon dioxide supply A, and a reflux condenser D. The latter leads to the washing bulbs E containing a mixture of nitric and sulphuric acids in molecular proportions and which serves to retain benzene from the gas which is then scrubbed free of acid fumes by passage through water. The nitrogen is finally collected over potash in the Schiff's nitrometer.

200 c c. of Fehling's solution are placed in B and covered with a layer of petroleum to prevent absorption of the carbon dioxide in the alkaline liquor The flask is heated on a water-bath and when all the air has been displaced by carbon dioxide a blank experiment is carried out using a known volume (10 ml) of standard phenylhydrazine solution (approx. 5%) together with aqueous sodium acetate (10%). This mixture is run in through the dropping funnel, the stem of which is filled with water and the funnel rinsed out with hot water. The nitrogen evolved is collected and measured. The experiment is now repeated using the same volume of the phenylhydrazine solution and aqueous sodium acetate to which has been added a known weight of the carbonyl compound. The difference in the volume of nitrogen now obtained is a measure of the carbonyl present in the substance (Watson Smith and Kauffler, Chem. News, 1906, 93, 83).

In some cases it is possible to evaluate the carbonyl group by estimating the amount of cuprous oxide formed in the above reaction. The oxide is filtered off, dissolved in standard ferric sulphate solution, and the ferrous sulphate produced is titrated with $N/10$ potassium

permanganate (Smedley MacLean, Biochem. J. 1913, 7, 611).

Alternatively, uncondensed phenylhydrazine may be allowed to react with excess of $N/10$-iodine solution which is then back-titrated with thiosulphate:

$$C_6H_5\cdot NH\cdot NH_2+2I_2=3HI+C_6H_5I+N_2$$

ESTIMATION OF NITRO- GROUPS.—This radical is usually determined by reducing it to the corresponding amino-group either with standard stannous chloride or titanous chloride solutions. The latter method is, perhaps, the more commonly employed and a brief description of it is given.

The titanous chloride, of about $N/30$ strength, is made up by boiling 50 ml. of commercial 20% solution with 100 ml. of hydrochloric acid, cooling, and diluting to 2¼ litres. This is stored in a bottle connected with a burette and an atmosphere of hydrogen is maintained throughout the apparatus. *The solution is standardised* by means of a ferric salt solution using potassium thiocyanate as the indicator, a relatively large amount of the latter being necessary to produce a sharp end point. The nitro- compound, if not soluble in water or hydrochloric acid, may be dissolved in alcohol although in this case a blank experiment must be made to correct for any reducing action of this solvent. Alternatively, substances insoluble in water may be rendered soluble by sulphonating with fuming sulphuric acid. Whichever method is adopted the nitro- solution is made up to approximately $N/30$, a known volume taken, and this reduced with excess of titanous chloride by boiling for 5–10 minutes in an atmosphere of carbon dioxide. After cooling, the excess of the reductant is estimated by titrating with standard ferric alum solution. From the equation

$$6TiCl_3+RNO_2+6HCl =6TiCl_4+R\cdot NH_2+2H_2O$$

the percentage of nitro groups present may be calculated :

$$1 \text{ ml. of } 0{\cdot}03N\text{-}TiCl_3=0{\cdot}23 \text{ mg. } NO_2.$$

AZO GROUPS.—Titanous chloride may also be used to estimate azo groups, especially in dyestuffs, and in many cases these act as their own indicator, being decolorised on reduction. For this purpose it is necessary that the dye be soluble in dilute hydrochloric acid, otherwise the indirect method used for nitro-groups must be adopted:

$$RN{:}NR'+4TiCl_3+4HCl =RNH_2+R'NH_2+4TiCl_4$$

ESTIMATION OF ORGANIC AMINES.—Amines are divided into three classes, primary, secondary and tertiary, depending on whether the nitrogen atom is linked respectively to one, two or three organic radicals, these being either aliphatic or aromatic groups. The nature of the attached groups governs largely the reactions of each of these classes and also influences the strengths of the amines as bases.

PRIMARY AMINES, RNH_2.—All primary amines when heated in alcoholic solution with chloroform and caustic potash produce carbylamines (*iso*nitriles) RNC, which possess pungent, disagreeable odours.

All such amines also react with nitrous acid, but whereas with aliphatic bases there is an immediate formation of an alcohol with simultaneous liberation of nitrogen, aromatic amines first furnish diazo- compounds which decompose only slowly at room temperature although nitrogen is quickly evolved on warming. $RNH_2+HNO_2=ROH+H_2O+N_2$. In the case of alkylamines the nitrogen can be collected and measured, thus serving to estimate the proportion of amino group present. The procedure is carried out by adding sodium nitrite solution to a known weight of the amine dissolved in excess of hydrochloric acid, the evolved nitrogen is collected in a nitrometer after passing through ferrous sulphate and alkaline (Na_2CO_3) permanganate solutions which serve to remove oxides of nitrogen. There is less risk of contamination with these oxides if nitrosyl chloride be used, this reagent being made by adding fuming hydrochloric acid to 40% aqueous sodium nitrite.

Aromatic primary amines may be estimated by dissolving a weighed amount in excess of hydrochloric acid and titrating at 0° with standard sodium nitrite, the end point being reached when a drop of the liquor dropped on to starch iodide paper gives a blue colour. The nitrite solution may be standardised against sodium sulphanilate, ($NH_2\cdot C_6H_4\cdot SO_3Na\cdot 2H_2O$), *p*-toluidine, or potassium permanganate.

Primary aromatic amines may be determined in a mixture with secondary or tertiary amines by diazotising with an excess of sodium nitrite and coupling the solution with a known volume of standard R-salt solution. The dye is precipitated with salt, filtered, and the filtrate examined to see whether the R-salt or diazonium salt be in excess. The experiment is then repeated using more or less R-salt until the point is reached when neither R-salt nor diazo-compound appears in the filtrate.

ESTIMATION OF IMINO GROUPS IN SECONDARY AMINES.—A known weight of the material is acetylated by heating with a given weight of acetic anhydride either alone or admixed with dry xylene, dimethylaniline, or pyridine, the reaction being carried out in a flask fitted with a reflux condenser. Excess of the anhydride is then hydrolysed with water and the resulting acetic acid is titrated with standard alkali using phenolphthalein as indicator. In this way the weight of acetic anhydride required to acetylate the amine is found.

Tertiary amines and the quaternary ammonium salts do not exhibit the above properties, but all give characteristic salts, such as aurichlorides or platinichlorides which may be employed to determine the amount of basic nitrogen present. For this purpose the double salts are ignited and the resulting gold or platinum is weighed. In most cases these auri- and platini-chlorides have the general formulæ $RHCl\cdot AuCl_3$ and $(RHCl)_2\cdot PtCl_4$ respectively, so that one atomic proportion of gold or half an atomic proportion of platinum is equivalent to

one basic nitrogen atom. In certain cases salts of anomalous composition are met with and it is therefore desirable that the analysis of other suitable compounds such as chromates, thiocyanates, ferrocyanides, picrates, etc., should be undertaken. G. T. M., G. R. D.

CHROMATOGRAPHIC ANALYSIS.

Chromatographic analysis is a method of separating mixtures of organic compounds by allowing a solution to percolate through a *vertical column of a suitable adsorbent, on which* the individual components are adsorbed with varying degrees of fastness. The column is then washed with the pure solvent (developed), *when the less easily adsorbed compounds* gradually move further down the column, until, in the ideal case, each component of the mixture occupies a definite zone; these can then be isolated and the adsorbed material recovered by extraction with a suitable solvent (elution).

The method thus takes advantage of the fact that differences in structure often have a much greater effect on the adsorbability of compounds than on their solubility; the term "chromatographic" was applied to it because it was originally employed to separate mixtures of natural pigments, which form coloured zones on the adsorbent, but it is of very wide application and affords an extremely delicate means of separating even closely related compounds whilst experimental losses are very small.

The apparatus illustrated in Figs. 1a–1c and 2 is suitable for small-scale work:

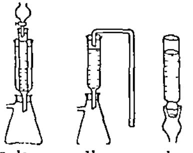


FIG. 1a 1b 1c

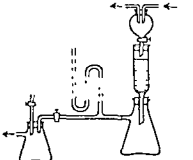


FIG. 2.

(From J.S.C.I., 1936, 55, 725.)

10–20 cm. lengths of narrow glass tubing filled with adsorbent resting on a plug of cotton *wool kept in place by a restriction near the* bottom of the tube are convenient for micro-work and A. Winterstein (Z. physiol. Chem. 1933, 220, 263) has designed apparatus for handling larger quantities; it is, however, sometimes convenient to perform a large-scale separation by employing a large number of small tubes (Zechmeister and Cholnoky, Annalen, 1935, 516, 37). For experimental details, *see* the reviews quoted below.

Although a mixture of unknown composition may require preliminary tests to decide the most suitable adsorbent, aluminium oxide is generally quite successful. Even commercial grades are often serviceable (Koschara, Z physiol. Chem. 1936, 239, 89), although these vary in adsorptive power and may contain an appreciable amount of alkali; for this reason it is advisable to use the special standardised products such as Merck's "Aluminiumoxyd nach Brockmann" Other useful adsorbents are powdered *sugar, calcium hydroxide* and carbonate, magnesium oxide, and mixtures of these As solvents for the primary adsorption, petroleum, benzene, water, ether, chloroform, *and carbon disulphide have been employed,* whilst pyridine, alcohol and acetone are more often suitable as eluting agents.

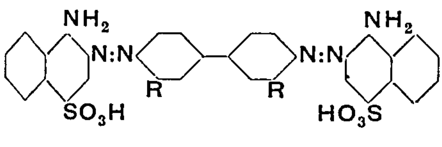
The chromatographic method was first used *by Tswett (Ber. deut. bot. Ges 1906, 24, 316)* and to a small extent by Willstätter ("Chlorophyllbuch," Berlin, 1913, p. 157). With the exception of a few references in the literature (*e g.* Palmer and Eccles, J. Biol. Chem. 1914, 17, 191; Coward, Biochem J. 1924, 18, 1114) the method was abandoned until the present decade, when R. Kuhn and his co workers achieved remarkable results in the field of carotenoid pigments (for a summary of the earlier results, *see* Willstaedt, Svensk Kem. Tidskr. 1936, 48, 32), since when chromatographic analysis has become the standard method of examining lipochrome pigments from the most varied sources, such as human fat, blood serum, etc. With extremely sensitive materials such as the carotenoids, even chromatographic adsorption may lead to isomerisation, as in the conversion of β carotene to ψ-α-carotene on *repeated adsorption on alumina (Gillam and* el Ridi, Biochem. J. 1936, 30, 1735).

The method has been applied with complete success to the separation of many other natural pigments, such as anthocyanins, α- and β-chlorophyll, the pigments of bile, fungi, bacteria, etc. Of particular interest are those cases where the analysis was performed in aqueous solution (flavines, thiochrome, *corpus luteum* pigments, dyestuffs, urine porphyrins).

In the instances cited above the colour of the pigments makes the demarcation of the adsorption zones easy, but any other simple qualitative test for the presence of an adsorbed compound may serve the same purpose even *though colour* is lacking. Heteroauxin was thus isolated by using a sensitive colour test (Kögl and co-workers, Z. physiol. Chem. 1934, 228, 90), whilst *it is sometimes possible to convert the* compounds under examination into coloured derivatives such as dinitrobenzoates or dinitrophenylhydrazones (Strain, J. Amer. Chem. Soc. 1935, 57, 758). *Brockmann (Z. physiol.* Chem. 1936,

241, 104) has isolated vitamin D from tunny-liver oil by an ingenious application of the chromatographic method, in which a coloured indicator of approximately the same adsorbability as the vitamin was added to assist in following the separation. A distinctive fluorescence, especially in ultra-violet light, is a considerable aid when working with aromatic compounds (ultra-chromatography), and Karrer and Nielson (Zangger Festschrift, Zürich, 1934, 954) and Winterstein and co-workers (Z. physiol. Chem. 1934, **230**, 148, 158, 169; Ber. 1935, **68**, [B], 1079) have achieved some striking separations in this way. It is sometimes possible to effect a separation without any such aid in cases when the components of a mixture differ very markedly in their adsorptive capacity, as in the mixtures of hydrocarbons and ketones examined by Winterstein (*l.c.*); Mark and Saito (Monatsh. 1936, **68**, 237) have applied the method in this way to the fractionation of highly polymerised materials (acetyl cellulose).

Of the recorded failures of the method to effect a separation may be quoted that of Kuhn and Grundmann (cited by Winterstein, Z. physiol. Chem. 1934, **230**, 263) with a mixture of bixin dialdehyde and the corresponding aldehydo-acid, and that of Ruggli and Jensen (Helv. Chim. Acta, 1935, **18**, 624) with a pair of dyestuffs of the formula:



one of which had R=H and the other $R=CH_3$, although another very similar pair of compounds could be separated without difficulty.

Among general reviews on the subject may be mentioned: A. Winterstein, "Handbuch der Pflanzenanalyse," Wien, 1933, iv, 2; Willstaedt, *l.c.*; Lederer, Chim. et Ind. 1935, **33**, 1072; Zechmeister and Cholnoky, Monatsh. 1936, **68**, 68, and "Die Chromatographische Adsorptionsmethode," Wien, 1937; A. H. Cook, J.S.C.I. 1936, **55**, 724. G. A. R. K.

QUANTITATIVE MICROANALYSIS.

Quantitative microanalysis relates properly to estimations carried out on very small samples (say, from 0·5 mg. to some 20 mg., but usually about 5 mg.) of initial material, using a microchemical balance capable of weighing to about a thousandth of a milligram. It is thus a special process in cases where only small samples are available; and, in the general case, an alternative to the older macroanalysis, which employs a sample some fifty times heavier and makes use of a balance sensitive to about a tenth of a milligram. Analysis at a stage intermediate between these employs a sample of some 20 mg. to 50 mg. and is referred to as semimicroanalysis; whereas at the stage of highest refinement with a sample of a few thousandths of a mg. (a few μg.), it is termed ultramicro-analysis. These last two processes are comparatively undeveloped.

Quantitative microanalysis is essentially the application of the ordinary methods of chemical analysis on a reduced scale; in many cases the details of the micro- and macro- processes are closely similar, although in others, improvements, modifications, or new methods have been introduced. The more accurate of the older methods are surprisingly readily adaptable to the micro-scale, offering a field for investigation which is still wide. Apart from the fact that it makes possible the examination of biological and other materials available only in very small quantities, micro-analysis is probably in general rather more accurate than the older process and possesses marked advantages over it in respect of ease of working, time required, bench space occupied by the apparatus, and cost of chemical reagents and of power. For these reasons it is increasingly replacing the macro-method in work of academic character and even in industrial chemistry. The chief disadvantages of the reduced scale are the higher cost of the micro-chemical balance and the greater care required in sampling, testing of reagents, and manipulation. The technique of microchemistry may be acquired with ease by anyone used to chemical analysis.

The production of a simple, invariable and durable chemical balance, weighing to about 0·001 mg., with a load up to 20 g., was achieved by W. H. Kuhlmann of Hamburg in 1912. F. Pregl, and also F. Emich, in Graz, Austria, were enabled by means of this balance to develop to the present microanalytical stage the small-scale methods of organic and inorganic analysis which they had already initiated with a less sensitive Kuhlmann balance. Pregl's work is more especially associated with the fundamental determinations of the elements in organic compounds and is justly renowned, whilst that of Emich relates chiefly to inorganic and general chemistry and is not so well known as it deserves to be. Only a few of the methods worked out by them, by their collaborators, and by others can be mentioned here. In all cases the literature must be consulted for the fuller details of apparatus and manipulation.

The Microchemical Balance.—For an account of some of the forms of this instrument now available (*v.* BALANCE, *also* Bibliography). Experience shows that the ordinary precautions suffice for the setting up and use of a microbalance; operation of the instrument is as simple and rapid as with an ordinary chemical balance. Microbalances are usually short-beam balances of the Bunge type, improved by the careful grinding and setting of the knife-edges and by increasing the rigidity of the beam; they require little attention during years of use. With regard to the maintenance of the standard weights, *see* J. J. Manley, Phil. Mag. 1933, (vii), **16**, 489. A. E. Conrady has described a method of employing an ordinary analytical balance as a microbalance, by providing a simple brake arrestment for the pointer (*v.* BALANCE, The Conrady Method of Weighing; W. H. J. Vernon, Chem. and Ind. 1934, **53**, 211; F. Emich, Abderhalden's "Handbuch der biologischen Arbeitsmethoden," Sect. I, Pt. 3, 183). W. H. Kuhlmann (*see* C. Weygand, reference (3) in

Bibliography) and others have constructed ultra-microbalances (*see also* E. Wiesenberger, Mikrochemie, 1932, 10, 10).

In weighing apparatus with the microchemical balance, tares are usually employed so as to avoid the too frequent handling of standard weights and to obviate volume corrections. Thus, in general, the differences of weight observed in analysis are read in *milligrams and fractions from the rider-scale* and pointer-scale of the balance. Convenient tares are small glass bottles containing fine lead shot, or suitably bent lengths of thick aluminium wire. These counterpoises are kept with the weights in the balance case, so that their weight is practically invariable if weighings are made within the same day. For difference weighings the desiderata are constant conditions of temperature, pressure, and humidity *within the balance room*; only in very rare cases do changes in the weather cause appreciable errors during one day, provided that the balance case is not exposed to direct sunlight. The effect of surface occlusion of moisture on objects weighed is usually negligible when weight differences are observed, for the objects are brought to the same state at each weighing by cleaning the surfaces and allowing the same degree of moisture occlusion to be attained. Small objects (such as silica combustion boats, micro crucibles, etc.) are surprisingly constant in weight even over periods of weeks, unless ignited in free flames or exposed to solvent action Thus, within the limits of accuracy of microchemistry, humidity changes have only a very slight effect. Dust in the laboratory air is quite without effect, since it is easily excluded from reagents, from objects weighed, and from the balance case; the filtration of air sometimes adopted in microchemical laboratories is therefore superfluous. The precautions to be used in microchemical work differ, in fact, but little from those in ordinary good macrochemical *analysis.*

Determination of Carbon and Hydrogen.—The method of Pregl, elaborated during the years 1910 to 1916, is essentially a modification of Liebig's combustion method. This, the most difficult and certainly the most important of Pregl's methods, has probably not yet evolved to a final form. The substance (some 3 to 5 mg) is weighed into a small boat (of platinum, silica, or porcelain) and burnt with oxygen and air in a hard-glass combustion tube (about 400 mm. long and 10 mm. wide) provided with an oxidising and absorbing filling; the water (some 1 or 2 mg.) and carbon dioxide (some 8 or 10 mg) are collected in glass absorption tubes and weighed. The filling (Pregl's "universal filling") for the combustion tube consists of silver wool (to absorb halogens), lead peroxide (to absorb oxides of nitrogen), a choking plug of compressed asbestos (to control the gas flow), all kept at 190° by means of a short heating mortar, and a mixture of lead chromate (to absorb sulphur, etc.), and copper oxide; the arrangement of the filling is shown in Fig. 1. The absorption tubes are of the type shown in Fig. 2,

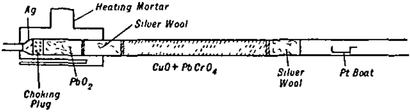


FIG. 1.

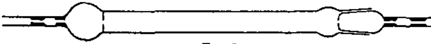


FIG. 2.

the essential feature being the terminal capillaries, which ensure constancy of weight when the tubes remain open to air for a quarter of an hour. They are sealed with a vapour-free cement at the stoppers. The entering gases are purified by means of a drying tube or train; their pressure is controlled by means of a simple gauge, and their volume is measured by a water-dropping flask (Mariotte flask) attached at *the exit end of the absorption tubes.* The Mariotte flask also enables suction to be applied to the tube system. The analysis takes about an hour from start to finish, and uses some 180 c.c. of gas; the volume of gas may be increased but must be kept constant in a series of analyses. Glass to glass connections are made as far as possible throughout; all rubber tubes used in the connections are freed from volatile substances, and are made non-permeable by impregnation with paraffin wax. Gas heating of the combustion tube is usual, but electrical devices have been employed. It must be understood that numerous modifications of Pregl's apparatus have been proposed or are in use. Pregl used calcium chloride and soda lime in the drying and absorption trains, but this necessitates frequent refilling of these tubes (according to Pregl, after every five or six analyses). *More efficient modern substitutes* are phosphorus pentoxide on glass wool, or magnesium perchlorate ("anhydrone"), for the calcium chloride, and caustic soda on asbestos granules ("ascarite" or "natronasbest") for the soda lime; the absorption train then serves for at least 20 analyses and the drying train for about 100. Owing to the vapour pressures of the hydrates of calcium chloride, this substance has many disadvantages;

phosphoric oxide, the best desiccating agent, was substituted for it by G. Kemmerer and L. F. Hallett in a rapid-flow apparatus for the microanalysis of lake deposits (*see* Ind. Eng. Chem. 1927, **19**, 173, 1352), and was later used by H. D. K. Drew and C. R. Porter (J.S.C.I. 1928, **47**, 17T) in the Pregl apparatus. The latter authors showed that the Pregl combustion tube after thorough desiccation absorbs water during the combustion of a substance containing hydrogen and only slowly liberates it even to perfectly dry gas. The tube is therefore not an "absolute" tube and analyses can only be carried out in succession after the tube has attained a "normal" state; this is ensured by first thoroughly burning out the tube and then performing one combustion, which is neglected. Thereafter, if the tube, when not in use, be kept efficiently sealed with a phosphorus pentoxide stopper-tube, successive analyses can be correctly carried out. For the maintenance of the normal state, it is essential that the cold tube should never be open to the atmosphere; it is best, therefore, to keep the tube, when not in use, under a slight permanent pressure of dry air or oxygen. It should then remain permanently in the "normal" state. For the equilibria in the apparatus, the foregoing paper (Drew and Porter) may be consulted, together with the following works: M. Boëtius, "Uber die Fehlerquellen bei der mikroanalytischen Bestimmung des Kohlen- and Wasserstoffes," Verlag chemie, G.m.b.H., Berlin, 1931; J. Lindner, "Mikro-massanalytische Bestimmung des Kohlenstoffes und Wasserstoffes mit grundlegender Behandlung der Fehlerquellen in der Elementaranalyse," Verlag Chemie, G.m.b.H., Berlin, 1935. Practically all classes of organic substances can be estimated in the Pregl apparatus, including organo-metallic compounds. The accuracy is the same as that in the most efficient macro-methods.

Methods for determining carbon in the wet way, using sulphuric acid and potassium dichromate to effect preliminary decomposition, have been described (*e.g.* H. Lieb and H. J. Krainick, Mikrochemie, 1932, **10**, 99).

Determination of Nitrogen.—(1) *Pregl's Micro-Dumas Method.* This method closely resembles the macro-method. It is valid for most types of substances, though difficult cases occur where the substance requires prolonged heating in order to set free all the nitrogen. The powdered substance (some 5 mg.) mixed with fine copper oxide is burnt in a stream of pure carbon dioxide from a Kipp's apparatus in a combustion tube, identical with that just described but containing coarse copper oxide and also a length of reduced copper. The nitrogen produced (about 0·5 c.c.) is collected over 50% potash solution in a small azotometer. The reduced copper, which removes the oxygen from any oxides of nitrogen, is placed well within the tube, so that the gas, after passing it has to traverse a layer of hot copper oxide which is becoming cooler towards the azotometer: this serves, it is supposed, to reoxidise any carbon monoxide generated by the action of the hot copper upon the carbon dioxide (on the effect of traces of iron or zinc in the reduced copper, *see* Cherbuliez, Helv. Chim. Acta, 1920, **3**, 652). The analysis takes about an hour and the results are very accurate. The main theoretical weakness of the method lies in the fact that 2% of the volume of nitrogen read must be subtracted in order to compensate for the volume of the potash solution adhering to the azotometer tube, for the vapour tension of the potash solution, and for nitrogen occluded in the copper oxide. Although the correction cannot thus be strictly proportional to the volume of gas, it appears to be sufficiently accurate when, as is usual, the volume is near 0·5 c.c. This method of analysis, which is adaptable to the cases of liquids also, is readily mastered. In some cases it is possible to apply it in the absence of a microbalance, by making up a solution of the given substance (0·1 g.) in a solvent like carbon tetrachloride, mixing an aliquot part with copper oxide and allowing the solvent to evaporate (J. B. Niederl, O. R. Trasitz and W. J. Saschek, Mikrochemie, Emich Festschrift, 1930, **219**, 232).

(2) *The Micro-Kjeldahl Method.*—Little need be said of this useful method, since it closely resembles the macro-method. It has the advantage over the latter that the preliminary decomposition with sulphuric acid to give ammonium sulphate usually occupies a much shorter time, particularly if a few drops of hydrogen peroxide are employed at intervals in addition to the usual reagents. The distillation of the ammonia is conducted in a compact apparatus of the Parnas and Wagner type

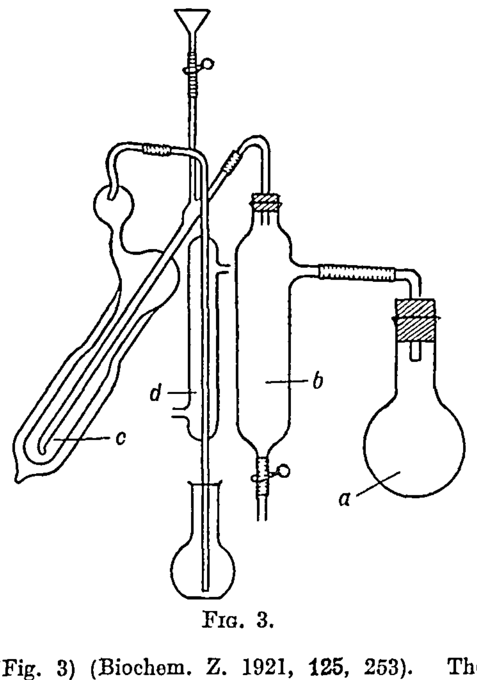


FIG. 3.

(Fig. 3) (Biochem. Z. 1921, **125**, 253). The process is subject to much the same disabilities as the macro-method, failing with certain types of compounds (*e.g.* nitro-compounds, hydrazine derivatives) unless preliminary reduction is effected. According to A. Friedrich (Z. physiol. Chem. 1933, **216**, 68) this is most conveniently carried out by heating with hydriodic acid;

case of this element the nitric acid must be removed by evaporation and the subsequent precipitation of tellurium completed in the presence of hydrazine hydrochloride (H. D. K. Drew and C. R. Porter, J.C.S. 1929, 2091). These methods are adaptations of those used on the macro-scale.

Determination of Phosphorus.—The available methods are similar to those used in macro-analysis: the phosphorus is transformed to phosphoric acid by oxidation, either in the wet way with nitric and sulphuric acids or by fusion with sodium carbonate–sodium nitrate; the phosphorus is preferably determined gravimetrically as ammonium phosphomolybdate, or it may be determined volumetrically.

For the decomposition with acids, the sample is heated with about 0·5 c.c. of concentrated sulphuric acid containing a few drops of concentrated nitric acid, until a clear solution is obtained; occasional addition of a few drops of aqueous hydrogen peroxide to the cooled vessel hastens the decomposition. The decomposition by fusion may be effected in a platinum vessel placed in a hard-glass tube heated in a slow current of oxygen. Precipitation of the ammonium phosphomolybdate is carried out under standardised conditions (*see* R. Kuhn, Z. physiol. Chem. 1923, **129**, 64); it may be collected upon an asbestos filter, washed finally with acetone or ether, and dried in a vacuum. The weight of phosphorus is obtained from that of the phosphomolybdate by multiplying by the factor 0·0145 (N. von Lorenz, Z. anal. Chem. 1912, **51**, 161). The phosphomolybdate precipitate may be determined volumetrically by dissolving it in excess of dilute standard caustic soda, boiling off the ammonia, and determining the excess of alkali in the presence of phenolphthalein (*see* Biochem. Z. 1920, **104**, 23).

Determination of Arsenic.—This can be effected, according to Pregl, by preliminary decomposition to arsenic acid in a micro-Carius tube with nitric acid, followed by precipitation of the arsenic as magnesium ammonium arsenate, collection upon a micro-Neubauer filter, and ignition to magnesium pyroarsenate $Mg_2As_2O_7$. Decomposition of arsenic compounds can also be effected with sulphuric acid and hydrogen peroxide in an open vessel, as for phosphorus compounds. O. Wintersteiner estimates the arsenic acid volumetrically by reduction with hydriodic acid and titration of the liberated iodine (Mikrochemie, 1926, **4**, 155).

The Micro-Determination of Metals.—Pregl showed that, where they are unaccompanied by other non-volatile constituents, many metals can be determined by simple ignition with sulphuric acid or with nitric acid, or both, in a suitable boat or crucible, heated in a stream of air or other suitable gas maintained in a bent hard-glass tube ("micro-muffle"). This method is extremely useful and accurate; thus, the alkali and alkaline-earth metals, manganese, cobalt, and other metals can be determined as sulphates; copper, aluminium, iron, tin, and others as oxides; and palladium, platinum, and gold as the free elements. Analysis may sometimes be performed with less than 1 mg. of material.

For separation and determination of metals, *see* Emich (*op. cit.*) and, in general, Mikrochemie publications. Only a few typical instances will be mentioned here.

(*a*) The classical methods of macro-analysis, in inorganic as well as in organic work, may, often readily, be adapted to the micro-scale by careful attention to detail. As an example, the microanalysis of a mineral beryllium silicate, in which the beryllium, magnesium, aluminium, iron, and phosphorus were determined by A. Benedetti-Pichler and F. Schneider (Mikrochemie, Emich Festschrift, 1930, 1) may be consulted. The simultaneous micro-determination of platinum and potassium and also of iridium and potassium can also be effected by simple methods (H. D. K. Drew, H. J. Tress, and G. H. Wyatt, J.C.S. 1934, 1787); whilst many other instances may be found in the literature.

(*b*) The quantitative separation of metals by special organic precipitants is often applicable on the micro-scale. Some examples are: the precipitation of *copper* by means of α-benzoin-oxime (R. Strebinger, Mikrochemie, 1923, **1**, 72); that of *thorium* by means of picrolonic acid (F. Hecht and W. Ehrmann, Z. anal. Chem. 1935, **100**, 87); *zinc* by means of quinaldinic or anthranilic acid (P. R. Rây and M. K. Bose, Mikrochemie, 1935, **17**, 11; **18**, 89; C. Cimeran and P. Wenger, *ibid.* 1935, **18**, 53); *bismuth* by means of pyrogallol (R. Strebinger and E. Flaschner, *ibid.* 1927, **5**, 12).

(*c*) Electro-analysis (*e.g.*, the determination of *copper* by Pregl, and that of *mercury* by A. Verdino, *ibid.* 1928, **6**, 5) and nephelometry (*e.g.* for *mercury* by S. I. Sinjakova, Z. anal. Chem. 1935, **100**, 190; and for *aluminium* by P. Meunier, Compt. rend. 1934, **199**, 1250) are sometimes applicable on the micro-scale.

Volumetric Work.—Pregl and others have shown the feasibility of carrying out titrations with very small quantities of liquids and have described micro-burettes with capacities ranging from 0·1 c.c. to 10 c.c., with deliveries ranging from less than 0·0001 c.c. to 0·01 c.c. (for details, consult Pregl's book, and, *e.g.*, Biochem. J. 1925, **19**, 270; Mikrochemie, 1933, **13**, 1). The volumetric micro-methods have been used in alkalimetry, acidimetry, iodimetry, and numerous other processes, among which the determination of carboxyl (Pregl) and of amino-acids (W. Grassman and W. Heyde, Z. physiol. Chem. 1929, **183**, 32) may be mentioned. Some of the volumetric processes have already been referred to in the foregoing sections.

Determination of Special Groupings in Organic Compounds.—The Zeisel method for the estimation of *alkoxyl groups*, particularly methoxyl, is readily reduced to the micro-scale, with a great improvement in accuracy and rapidity; in addition, only about 2 c.c. of hydriodic acid is required for a determination. The gas is washed by a suspension of red phosphorus in water; or, better, by aqueous sodium thiosulphate containing cadmium sulphate (*see* Z. physiol. Chem. 1927, 163). Pregl has described elegant apparatus for the purpose (Fig. 5) in which the decomposition vessel and the washing chamber are sealed together; gravimetric or

volumetric determination of the evolved alkyl iodide may be made (*see* Pregl's work, and also Monatsh. 1915, **36**, 853). Glycerol can be determined as *iso*-propyl iodide. Methoxyl and ethoxyl can be determined simultaneously (Z. physiol. Chem. 1923, **127**, 190). It should be noted that the estimation of methoxyl sometimes fails in the presence of sulphur; but certain aromatic sulphonic acids have been found to give correct values

Methylimino Groups can be estimated by a method worked out by Pregl and his pupils, which is essentially similar to the foregoing process but is conducted more vigorously. *Acetyl* and *benzoyl* groupings can also be determined. By measured saturation with hydrogen, R. Kuhn and others have determined *double bonds* present in organic compounds (*e.g.* Angew. Chem. 1934, **47**, 145, J. pr. Chem. 1935, [ii] **143**, 3). For the determination of

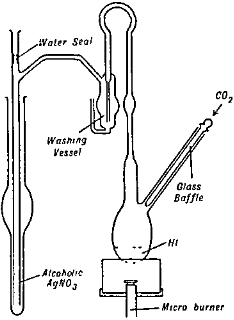


FIG. 5.

iodine values, see J Boeseken and P. Pols, Rec. trav. chim. 1935, **54**, 162.

Physical Determinations.—Many micromethods for physical determinations have been described, of which only a few examples will be given. The boiling-point of a solid or liquid, up to about 250°, can be determined with an accuracy of 1° using as little as 2–5 mg. of the substance, according to H. Roth (*l.c.*, p. 225). F. Emich describes methods for fractionating mixtures of a few drops of each of two liquids and determining the boiling points. Determinations of density, optical rotatory power, and molecular weight can be made on 10 mg. or less of substance. For the determination of molecular weight, the Rast and the Barger method has been employed; but the most important method is that of F. Pregl and H. Lieb, which makes use of a micro ebullioscopic apparatus of the Beckmann type, in which 1·5 c.c. of solvent is heated by means of a micro-burner; this method and also the electrical method of boiling small quantities of solvents are subject to some uncertainty owing to the difficulty of eliminating superheating effects.

Concluding Remarks.—The work on microchemical analysis during the past 25 years has shown that a large number of the standard methods of analysis can be carried out with equal accuracy, and with greater ease and elegance, on the mg. scale; and, in fact, there is little reason to anticipate that any of them is incapable of such transformation. The tendency in the future will doubtless be in the direction of a still further reduction of scale, into the region where the accurate analysis of very minute particles of matter may be expected to afford invaluable information to the biologist. Here, however, it may be predicted with some confidence that far greater changes of technique will be necessary, for it is probable that some of those fluctuations (for example the humidity effect) which are of secondary importance in micro-chemical measurements may become prime considerations in the submicrochemical region.

Bibliography—(1) F. Pregl, "Quantitative Organic Microanalysis" (transl by E. Fyleman), J. & A. Churchill, London, 1924; (2) a further edition of the foregoing H. Roth, "Quantitative Organic Microanalysis of Fritz Pregl" (transl by E. B. Daw), J. & A Churchill, London, 1937; (3) C. Weygand, "Quantitative analytische Mikromethoden der Organischen Chemie," Akad. Verlags Gesellschaft m b.H. Leipzig, 1931; (4) A. Friedrich, "Die Praxis der quantitativen organischen Mikroanalyse," Franz Deuticke, Leipzig, 1933; (5) F. Emich, "Lehrbuch der Mikrochemie," 1926, and "Mikrochemisches Praktikum," 1931, J. F. Bergmann, Munich; (6) G. Klein and R. Strebinger, "Fortschritte der Mikrochemie in ihren verschiedenen Anwendungsgebieten," 1927, F. Deuticke, Leipzig. H. D. K. D.

VOLUMETRIC ANALYSIS.

In this type of analysis the proportion of an ingredient is found not by weighing the substance or a derivative, but by determining the volume of a solution of known concentration required to complete some particular reaction, such as neutralisation, oxidation, or precipitation. This completion is usually indicated by a change of colour, by the coloration of a colourless solution, or by the formation of a permanent precipitate. In many cases a third substance is added in order to make such changes readily detectable, and this is called an *indicator*. It is an internal indicator if it is added to the liquid being titrated, or an external indicator if drops of this liquid are withdrawn and brought into contact with it. The use of the latter type of indicator, being somewhat tedious, is avoided if possible.

Only those reactions can be used for volumetric purposes which are rapid, simple, and definite, with no possibility of side-reactions. Moreover, the reaction should proceed quantitatively at any ordinary concentration. The reaction used to denote the end-point should

be rapid, decisive and sensitive, so that the minimum excess of the reagent should suffice to cause it.

For volumetric processes it is necessary to have accurately graduated flasks, pipettes and burettes. The flasks should be fitted with well-ground stoppers, and should have relatively long and narrow necks, the graduation being below the middle of the neck in order to afford sufficient free space for efficient shaking. Flasks graduated to *contain* various volumes are obtainable, those of 2,000, 1,000, 500, 250, 200, and 100 c.c. being the commonest; these bear the letter C near the graduation mark; but occasionally one requires a flask to *deliver* a specified volume, and these bear the letter D. Those of the latter type are calibrated so that the exact volume is delivered if 30 seconds' drainage is allowed after the continuous flow has ceased.

A pipette is usually a cylindrical bulb terminating at each end in a tube, the lower of which is drawn out to a jet. The flow of liquid is adjusted or stopped by the pressure of a finger on the top. Pipettes are almost always calibrated for delivery; the usual type has only one mark corresponding to a definite volume, but pipettes are also used which consist of a long uniform length of tube calibrated throughout most of its length, one end being drawn out to a jet.

A burette is a long tube of uniform bore, 12–15 mm. wide, graduated in cubic centimetres (c.c.) and tenths. The commonest capacity is 50 c.c. The tube is open at the top, but at the lower end it is constricted and attached to a tap. The latter may be prevented from sticking by a trace of vaseline, and from slipping out by a thin rubber band passing over it and round the burette tube. If hot liquids are to be titrated it is advisable, in order to avoid heating the burette and its contents, to use a burette of which the part carrying the stopcock is bent twice at right angles, so that the main part is not directly over the hot liquid.

When a burette is in use it should be kept vertical, and a test-tube inverted over the top is a useful device to prevent access of dust. Burettes, and all other graduated vessels, should be kept free from grease by frequent treatment with cold chromic acid solution in fairly concentrated sulphuric or nitric acid, which is allowed to stand in them overnight.

Standard solutions should be kept in well-stoppered bottles in a cool place and protected from direct sunlight. When many determinations of the same kind have to be made, it is convenient to keep the reservoir of standard solution attached to the burette to facilitate the filling. A glass T-piece is introduced between the graduated part of the burette and the tap, and is attached by a rubber tube to a tubulus at the bottom of the reservoir which contains the standard solution and stands on a shelf above the burette. The top of the reservoir should be fitted with a cork carrying a guard tube containing soda lime or other protective substance. The flow of liquid into the burette is regulated by a screw clip or pinchcock on the rubber tube. If the liquid acts upon rubber these connections must be constructed of glass and furnished with a tap. Burettes may be obtained fitted with three-way taps, so that they can be filled from the bottom by attachment to the reservoir, the tap connecting the burette either with the supply or with the outflow as required. This method has the advantage of avoiding the formation of air bubbles. A convenient method of filling from the bottom in the absence of a three-way tap is described in Chem. News, 1906, **93**, 71.

If the standard solution alters on exposure to air, the surface of the liquid may be covered with a layer of purified high-boiling paraffin, or the guard tube mentioned above may contain a suitable protective substance. Alternatively, the upper part of the stock bottle may be filled with carbon dioxide, and the top connected to a generator for the gas. When the solution is withdrawn the gas enters. If the nature of the solution permits, coal gas may be used in place of carbon dioxide.

Graduation of the Instruments.—Accurate calibration of the measuring vessels is essential if correct results are to be obtained, and all the instruments should be checked before being taken into use. Although it is sufficient for most purposes if the relative volumes of the vessels are correct, they should nevertheless be graduated in true cubic centimetres or millilitres (the difference of 28 parts per million is immaterial for most purposes). If the calibration is performed at a temperature of 15°–20°C., variations from the true volume resulting from the expansion of the glass are so small for the normal temperature changes of the laboratory that they may be neglected. The standard temperature for calibration in Great Britain is 15°C., but it is proposed to alter this to 20°C., which is the temperature employed in Europe and America and is more convenient in several respects.

The vessels are checked by ascertaining the weight of distilled water at a known temperature which they will contain or deliver, as the case may be. A large beaker of distilled water is boiled, rapidly cooled, and left in the balance room until it has attained temperature equilibrium. The vessels to be calibrated are thoroughly cleansed by successive treatments with concentrated potassium hydroxide, distilled water, and a warm concentrated solution of chromic acid in fairly strong sulphuric acid, and then rinsed well with distilled water. The flasks are then dried, and a narrow strip of paper is attached vertically to the neck of the flask above and below the mark; the flask is then placed on one pan of a large balance sensitive to about 10 mg. in the case of a litre flask or correspondingly less for smaller flasks, and counterpoised. Weights corresponding to the correct weight of water at the temperature concerned (*see* below) are then placed in the other pan, the flask is filled nearly to the mark with water, and water is added drop by drop until the balance is in equilibrium. Any water adhering to the inside of the neck of the flask is removed with filter paper. If the level of the water does not agree with the maker's mark, a pencil mark is made level with the lower edge of the meniscus, the glass above and below is thinly coated with

an even film of wax, and a horizontal ring is scratched through by means of a needle precisely level with the pencil mark. The ring is then *covered with a strip of filter paper moistened* with hydrofluoric acid, and after a few minutes the acid is washed off and the wax removed, leaving the etched ring.

Certain corrections which have to be applied, namely, those for the weight of air displaced by the brass weights and the liquid and the reduction of the volume to true cubic centimetres at 4°C., are allowed for in the following table, where x is the quantity which has to be subtracted from 1,000 to obtain the apparent weight in air (brass weights being used) of 1,000 c.c. of water at t°C. For example, at 18°C. the apparent weight of 1,000 c.c. is 1,000−2·43 =997·57 g.

t°	x	t°	x
0	1·19	16	2·09
1	1·13	17	2·25
2	1·09	18	2·43
3	1·07	19	2·62
4	1·06	20	2·82
5	1·07	21	3·03
6	1·09	22	3·26
7	1·13	23	3·49
8	1·18	24	3·73
9	1·25	25	3·98
10	1·33	26	4·24
11	1·43	27	4·52
12	1·53	28	4·80
13	1·65	29	5·08
14	1·78	30	5·38
15	1·93		

Flasks of other denominations are graduated similarly, the correction being proportional. Flasks marked for "delivery" are similarly calibrated; the water is emptied by slowly and carefully tilting the flask until it is empty, *draining it for 30 seconds*, and touching the lip against a wet glass surface.

In calibrating a pipette, and also in its use, it is essential to adhere to a standard procedure for emptying it: it should be held vertically with its point just touching the side of the receiving vessel, and allowed to drain for 15 seconds after the continuous flow has ceased. The last drop should on no account be blown out. The calibration is checked by filling the pipette to the mark with water at a known temperature, and delivering the contents into a stoppered, tared flask, which is re-weighed. From the mean weight of water thus obtained from several determinations, the true volume is calculated by means of the above table. If the error is considerable, a new mark must be made by finding the true volume corresponding to each of a series of pencilled marks made on a strip of paper, affixed as above, until the correct position is found, and then etching a mark.

The burette is most accurately calibrated by a succession of weighings of the water delivered at intervals of a few cubic centimetres, the burette being read between each, and corrections being applied to the weights as above. A simpler *method, which is not approved by the National* Physical Laboratory, is by use of a small pipette devised for this purpose by Ostwald. This should have a capacity of about 2 c.c., and is attached to the burette as indicated in Fig. 1. The burette and pipette are filled with water to the zero mark and to the mark a respectively, care being taken that no air bubbles are left in the tubes. The clip I, or the tap of the burette, is opened, and water allowed to run from the burette into the pipette till the level b is reached. The reading is then noted, and the pipette emptied to the mark a by opening clip II (or, better, a tap in the same place to avoid the use of rubber tubing). These operations are repeated until the burette reading is about 50 c.c. Suppose, for example, that after 24 fillings the burette reading is 49·49 c.c. The burette is now refilled, and exactly this volume of distilled water is run out into a tared flask, with all the precautions used in an actual titration, and weighed. From the above table the true volume of this water is calculated. Suppose this to be 49·44 c.c. Then the volume of the calibrating pipette must be 49·44/24=2·060 c.c. The differences between the successive burette readings and the numbers 2·06, 4·12, 6·18 . . . give the burette errors at these intervals, and a curve may be constructed to show these errors with their appropriate signs. In the foregoing example, the error at 49·49 c.c. is obviously −0·05 c.c.

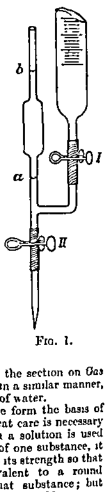


Fig. 1.

For another method of calibrating pipettes, *see* Morse and Blalock (Amer. Chem. J. 1894, 16, 479).

The burettes described in the section on *Gas Analysis* may be calibrated in a similar manner, mercury being used instead of water.

Standard Solutions.—These form the basis of all volumetric work, and great care is necessary in their preparation. When a solution is used only for the determination of one substance, it may be convenient to adjust its strength so that each c.c. is exactly equivalent to a round quantity, say 1 mg., of that substance; but for ordinary purposes it is preferable to use solutions made up on the *normal* basis. A *normal solution* contains in one litre the equivalent in grams of the active substance; for example, a normal solution of sulphuric acid contains 49·03 g. of the actual acid per litre. Solutions of lower concentration, such as *decinormal* or *centinormal*, contain respectively one-tenth or one hundredth of an equivalent per litre, a decinormal solution of potassium

permanganate containing 0·8 g. of active oxygen per litre.

A standard solution is usually made up approximately and then standardised against a weighed amount of some pure substance. It is usually made slightly too concentrated so that it can be accurately adjusted by dilution after standardisation, but if it is too weak or if the dilution is not favoured it is better to use a *factor* by which readings must be multiplied in order to convert them into equivalent readings of a normal or decinormal solution. For example, if 1 c.c. of potassium permanganate is found to be capable of oxidising 0·005630 g. of iron, as against 0·005584 g. for a decinormal solution, then the factor is 0·005630/0·005584= 1·008, and when using it to determine a substance of equivalent x, each c.c. of this permanganate will oxidise $1{\cdot}008x/10{,}000$ g. of the substance. When only, say, 2 litres of a solution are required and the pure reagent is available, the exact quantity may be weighed out, dissolved, and diluted to the required volume. Solutions of silver nitrate and potassium dichromate, for example, may thus be prepared.

Measurements.—In using pipettes or burettes, these must first be rinsed with distilled water and well drained, and then the operation repeated with a small quantity of the required solution and again drained, this portion of the solution being rejected.

The correct reading of the level of a liquid in a burette or pipette requires certain precautions. First, the instrument must be held vertically. Secondly, since ordinary liquids form a concave surface or meniscus, the reading should always be taken from the lowest point of this curve unless the liquid is very dark, and in this case the upper line of the surface must be taken. Thirdly, the meniscus must be properly illuminated, and must be on a level with the eye in order to avoid parallax. The best method of avoiding this error is by the use of a burette having the graduation marks at each cubic centimetre carried right round the tube, and those at each intervening half cubic centimetre half way round, as required by the National Physical Laboratory. In absence of such a burette, recourse may be had to Mohr's device of a piece of card one half of which is black and the other half white. This is attached to the burette by an indiarubber ring, and is adjusted so that the horizontal edge of the black half, which is the lower, is not more than 3 mm. below the meniscus. The lower edge of the curve then appears black against the white background. If the card is too low the reading will be slightly too high. Some burettes are provided at the back with a dark vertical line on a milk-glass background. When the eye is on a level with the bottom of the meniscus, the dark line appears to be drawn out to two fine points which just touch one another; such markings, however, are not accepted by the National Physical Laboratory for Class A burettes. By means of these devices accurate readings may easily be made without using a burette float, thus avoiding some disadvantages.

In addition to the errors common to all analytical processes, another error arises in volumetric analysis owing to the variations in the concentrations of solutions due to changes of temperature, a change of 5°C. making a difference of 0·1% in the case of $N/10$ solutions and still more in more concentrated solutions, especially those of acids and alkalis. The coefficients of expansion of certain standard solutions were determined by Schlösser, and corrections calculated from his results are tabulated for some liquids on p. 643.

Errors of the last type can be eliminated by weighing the solutions instead of measuring them. The liquid is contained in a "weight burette," a light glass bottle with a long jet-like neck and a tubulus at the shoulder which can be closed by the finger, thereby regulating the flow of liquid. The difference in the weight of the vessel before and after the titration gives the quantity of reagent used; a convenient weight burette devised by C. A. Kraus is described by Washburn (J. Amer. Chem. Soc. 1908, **30**, 31).

Volumetric methods may be broadly classified as: I. Methods of Saturation, *i.e.* Mohr's term for what is now called Neutralisation; II. Methods of Oxidation and Reduction; III. Methods of Precipitation. Methods of Class I are dealt with in the following section on Acidimetry and Alkalimetry, and those of the other two classes are dealt with later.

Acidimetry and Alkalimetry.

This type of volumetric analysis is of great technical importance. It is true that in pure aqueous solution the amount of acid or alkali can be determined by finding the specific gravity of the solution and referring to an appropriate table, and gravimetric methods are also usually available, but volumetric methods are often to be preferred on account of speed, and with care they may be made very accurate. In these operations the amount of acid or alkali is calculated from the volume of standard alkali or acid, respectively, required for neutralisation, the exact point of equivalence being determined by addition of a small quantity of an indicator.

Indicators.

Although until 1877 only natural colouring matters were available as indicators, these were gradually supplemented by synthetic indicators, *e.g.* methyl orange and phenolphthalein; and these have now been produced in such variety that, except for a few special purposes, the naturally occurring indicators are obsolete. In particular, indicators of the sulphonephthalein type are of great value for their brilliance and sharp colour change; one or other is available for almost any requirement, and they are strongly recommended.

In accordance with the ionic theory of solutions, acids may be divided roughly into two classes, "strong" and "weak," according as they are completely or only partly ionised in dilute aqueous solution. In the former case, the acid HM may be regarded as existing entirely in the form of the positive and negative ions, $H^{\cdot}$ and M' respectively; in the latter case, an equilibrium is set up between the ions and the

undissociated molecules: $H^{\cdot}+M'\rightleftharpoons HM$, so one has an equation

$$[H^{\cdot}][M']=K_a[HM],$$

where the symbols in brackets denote concentrations (g/l) of the respective ionic or molecular species, and K_a is a constant called the "dissociation constant." Most weak acids are so feebly ionised that $[HM]$ may usually without appreciable error be equated to the total concentration of the acid. Similar considerations apply, *mutatis mutandis*, to bases, so that $[B^{\cdot}][OH']=K_b[BOH]$ represents the ionisation of a weak base.

The water in all aqueous solutions is also very feebly ionised, $H^{\cdot}+OH'\rightleftharpoons H_2O$, so that $[H^{\cdot}][OH']=K[H_2O]$, but as the term $[H_2O]$ is always relatively very large and practically constant in dilute aqueous solutions, it is usual to replace the right hand side of the equation by a term K_w which is nearly equal to 10^{-14} at ordinary temperatures. Hence

$$[H^{\cdot}][OH'] = K_w \approx 10^{-14},$$

and in any aqueous solution this relation must always obtain between the concentrations of these two ions. (For simplicity, we ignore factors, such as salt effects, activities, the existence of $H^{\cdot}$ as $H_3O^{\cdot}$, etc.)

It had long been realised that the total concentration of an acid in aqueous solution did not afford a satisfactory criterion of the "acidity" of the solution, as judged, for example, by its solvent power or its catalytic effect. For instance, normal solutions of hydrochloric acid or acetic acid both neutralise the same volume of caustic alkali when titrated with phenolphthalein as indicator, yet the "acidity" of the former is greater than that of the latter by all ordinary standards. These apparent anomalies were seen to be largely accounted for by the Arrhenius theory of electrolytic dissociation (1887), for nearly all the hydrochloric acid is present as its ions, whereas only a small proportion of the acetic acid is thus ionised, the remainder of its acidic hydrogen becoming available as ions only on demand of the titrating alkali owing to the continuous displacement of the equilibrium $HC_2H_3O_2 \rightleftharpoons C_2H_3O_2'+H^{\cdot}$ towards the right as the existing hydrogen ions react. It is found, in fact, that a $0{\cdot}1N$- solution of acetic acid is only 1·35% ionised, so that $[H^{\cdot}]=0{\cdot}00135$, and it is now known that $0{\cdot}1N$-hydrochloric acid is virtually completely ionised, so that $[H^{\cdot}]=0{\cdot}1$.

p_H Convention.—It is often inconvenient to express very small hydrogen-ion concentrations as decimals, so Sörensen introduced the function p_H, defined as the logarithm of the reciprocal (to the base 10) of the concentration; hence $p_H=-\log_{10}[H^{\cdot}]$, and the convenience of this function becomes more apparent when we plot the change of $[H^{\cdot}]$ during the course of a titration of an acid by an alkali. Moreover, since $[H^{\cdot}][OH']=10^{-14}$, we have in pure water or in a perfectly neutral solution,

$$[H^{\cdot}]=[OH']=10^{-7},$$

or $p_H=7$ (and similarly $p_{OH}=7$).

HYDROLYSIS.—It is well known that aqueous solutions of salts of strong bases and weak acids react alkaline to many indicators. This is owing to "hydrolysis" by the water; for instance, sodium acetate is partly hydrolysed to sodium hydroxide and acetic acid, and as the former is completely ionised, and the latter only partly so, the OH' ions predominate over $H^{\cdot}$ ions, and hence when acid and base are present in exactly equivalent proportions, the solution is not neutral in the sense that $[H^{\cdot}]=[OH']=10^{-7}$ or $p_H=p_{OH}=7$; in fact, $p_H=8{\cdot}9$ for a $0{\cdot}1N$ solution of the salt. These remarks are illustrated in the scheme:

$$\begin{array}{ccc} NaC_2H_3O_2+H_2O \rightleftharpoons & NaOH \;+ & HC_2H_3O_2 \\ & \downarrow & \updownarrow \\ & \underbrace{Na^{\cdot}+OH'}_{\text{Complete.}} & \underbrace{H^{\cdot}+C_2H_3O_2'}_{\text{Partial}} \end{array}$$

Hence, in titrating acetic acid by alkali, one requires an indicator which is sensitive on the *alkaline* side of neutrality, and that is why phenolphthalein (useful range of $p_H=8{\cdot}3$–10) is suitable, but methyl orange (range 2·9–4·5) is useless. Similar considerations show that a weak base, on titration by a strong acid, requires an indicator changing on the *acid* side; *e.g.* $0{\cdot}1N$- ammonia shows a p_H of 5·1 when it has been treated with its exact equivalent of (*i.e.* has been "neutralised" by) $0{\cdot}1N$- hydrochloric acid, and so methyl red (range 4·2–6·3), but not phenolphthalein (8·3–10), is suitable.

All indicators in ordinary use are either weak acids or weak bases, which undergo a change in colour (owing to a change in molecular structure) on salt formation. Owing to the equilibrium involved between the two structural forms, these indicators cannot be treated as if they had a simple dissociation constant; nevertheless, each shows its colour change within a well-defined range of p_H, and a knowledge of this range is of great assistance in the choice of an indicator (*see* table on p. 640).

If we attempted to picture the course of neutralisation of, say, 10 c.c. of $0{\cdot}1N$- hydrochloric acid by $0{\cdot}1N$- sodium hydroxide by plotting the concentration of hydrogen ions as ordinates against the volume of added alkali as abscissæ, we should obtain a curve which fell almost linearly to the point corresponding to neutrality ($[H^{\cdot}]$ being negligibly small at $NaOH=10$ c.c.) and then continued along the zero line (axis of abscissæ) for excess additions of alkali. This, however, would tell us nothing about the state of affairs at the neutral point, and it is precisely here that it is most important to have information, particularly if either the acid or base being titrated is weak. Herein lies the great advantage of the p_H convention, for by its aid we can follow the course of the titration equally clearly throughout.

Characteristic curves for various types of titration are shown in Fig. 2, in which p_H instead of $[H^{\cdot}]$ is plotted against the volume of alkali added. The significant feature of these curves is that, unless both acid and base are weak or one of them is very weak, there is a well-marked vertical portion at the point corresponding to the addition of an exact equivalent of alkali; at this point, therefore, a small addition of alkali *produces a relatively large alteration of p_H* and

so would most readily cause colour change in an indicator. Further, the middle point of the vertical portion is *below* $p_H 7$ (*i.e.* on the acid side) for the case of a weak base and a strong acid (*cf.* ammonia and hydrochloric acid, above), and *above* $p_H 7$ (*i.e.* on the alkaline side) for the converse case. Moreover, a weak base and a weak acid show only a slight inflection at the point of equivalence,[1] so that it requires comparatively large additions of the base to produce a significant change in p_H, *i.e.* to produce colour change in an indicator; and similarly, a very weak acid (or base) gives only a very feeble inflection, so that in both these cases indicators are not capable of accurately denoting the end-point.

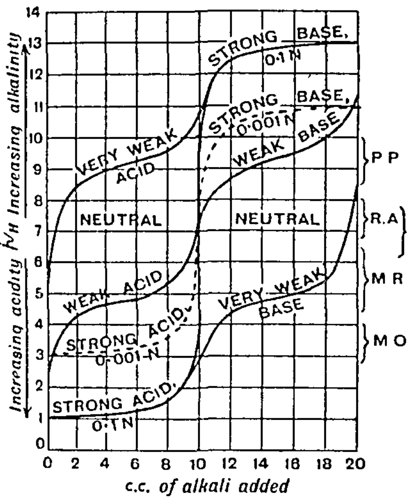


FIG. 2.

SELECTION OF INDICATORS.—The foregoing discussion, and deductions on similar lines, enable one to formulate rules for the choice of indicators, which may be briefly stated as follows (the converse titration being implied equally in cases i–iv):

(i) *Titration of strong base by strong acid*: any indicator of range between 3 and 10 provided the solution is not too dilute; as the solution becomes increasingly more dilute than $0{\cdot}1N.$, the indicator should have a range progressively nearer 6–8.

(ii) *Titration of strong base by weak acid*: an indicator of range above $p_H 7$, and the higher the weaker the acid, but *see* (v).

(iii) *Titration of weak base by strong acid*: an indicator of range below $p_H 7$, decreasing with decreasing strength of base; but *see* (v).

(iv) *Titration of weak base by weak acid*: this should be avoided if possible, as it can only be made accurate under special conditions.

(v) *Titration of extremely weak acids or bases*: this also requires special conditions; *e.g.* boric acid, phenol, or hydrocyanic acid gives salts which are so extensively hydrolysed that only indicators of an appropriately high (or low, for bases) and narrow range give any approach to an accurate titration (*see* under *Tropæolin O*, p. 641).

[1] This point is not, in general, at $p_H 7$; it happens to be so in the curve in the figure, because this is based on the case of acetic acid and ammonia, which are of approximately equal strength (*i.e.* $K_a \sim K_b$).

EFFECT OF CARBON DIOXIDE.—A factor which militates against the use of indicators of range above about 5·5 is that they are affected by carbon dioxide. In the presence of this gas or of carbonates, etc., it is therefore necessary either to use an indicator of range below that of methyl red (which is not appreciably affected by *traces* of carbon dioxide) or to boil off the gas while the titrated solution is still slightly acidic. For this reason, if the titration is being done by an acid in such circumstances, it is better to add an excess of the acid, boil the liquid, cool it, and back-titrate the excess of acid.

Other weak acids, *e.g.* hydrogen sulphide, cause similar complications.

INDIVIDUAL INDICATORS.—In the table on p. 640 are summarised the characteristics of selected indicators. Those of the sulphonephthalein type, given first, should be used in preference to others, for the reasons given on p. 637. These are followed by other synthetic indicators, and finally by natural colouring matters and substances of ill-defined constitution, which usually have neither such sharp colour changes nor such narrow ranges. Although indicators of the last class are practically obsolete, some of them (*e.g.* phenacetolin) serve a useful purpose in the hands of chemists who have had long experience with them.

In addition to those tabulated, an indicator which has been recently introduced (Wenker, Ind. Eng. Chem. 1934, **26**, 350) promises to be of great utility: "nitrazine yellow" (2′:4′-dinitrobenzeneazo - a - naphthol-3:6-disulphonic acid) has a very sharp colour change near the theoretical neutrality (yellow→blue at p_H 6·4–6·8).

For further information upon indicators and their use, *see* Prideaux, "The Theory of Indicators," 1917; Kolthoff and Furman, "Indicators," 1926; *idem*, "Volumetric Analysis," 1929; Sutton's "Volumetric Analysis," 1935; Walpole, Biochem. J. 1914, **8**, 628.

PREPARATION, ETC., OF INDICATORS.—The sulphonephthalein indicators are usually employed in about 0·1% alcoholic solution, and a few drops usually suffice for the titration of 100 c.c. of liquid. Details for other indicators follow in alphabetical order.

Cochineal.—The essential colouring matter of the dried female insect *Coccus cacti* Linn. is carminic acid; 3 g. of the substance (not pulverised) are extracted with 250 c.c. of 30% alcohol, and the clear liquid decanted. This indicator is of use in titrating ammonia, and is scarcely affected by carbon dioxide; the colour change is well defined even in artificial light. Cochineal is useless for titrating organic or other weak acids, and salts which are easily hydrolysed (*e.g.* those of iron, aluminium or copper) must be absent.

Congo Red.—A 1% solution in 30% alcohol is used, and one drop suffices for the titration of 20 c.c. of liquid. It is useful for the titration of alkaloids.

Iodoeosin (Tetraiodofluorescein, Erythrosin

TABLE OF INDICATORS.

Name.	p_H Range.	Colour change: acid→alkali.
Thymol blue	8·0–9·6	Yellow→blue (red at p_H1; yellow at p_H3).
Cresol red	7·2–8·8	Yellow→violet red
Phenol red	6·8–8·4	Yellow→red.
Bromothymol blue	6·0–7·6	Yellow→blue.
Bromocresol purple	5·2–6·8	Yellow→violet.
Bromocresol green	3·6–5·2	Yellow→blue.
Bromophenol blue	2·8–4·6	Yellow→violet.
Tropæolin O (resorcin yellow)	11·1–12·7	Yellow→orange.
Thymolphthalein	9·3–10·5	Colourless→blue.
Phenolphthalein	8·3–10·0	Colourless→red.
p-Nitrophenol	5·0–7·0	Colourless→yellow.
Methyl red	4·2–6·3	Red→yellow.
Congo red	3·0–5·0	Violet→reddish orange.
Methyl orange	2·9–4·5	Orange-red→orange-yellow.
Rosolic acid	6·9–8·0	Yellow→red.
Litmus (purified)	5·0–8·0	Red→blue.
Cochineal	4·8–6·2	Yellow→lilac
Lacmoid	4·0–6·2	Orange red→violet.
Phenacetolin	3–6 10–12	Yellow→pink→pale yellow (*see* p. 641).

B).—This is not an indicator in the ordinary sense, but was introduced by Mylius and Forster (Ber. 1891, 24, 1482) primarily for detecting extremely minute traces of alkali; 0·5 g. of the sodium derivative is dissolved in 1 litre of water, and 2·5 c.c. are added to the liquid to be tested together with 5 c.c. of chloroform or ether. The mixture is vigorously shaken during a test; in alkaline solution the aqueous layer is rose red, but in acid solution the aqueous solution is colourless and the organic layer assumes a yellowish tint. With this indicator N/100 or even N/1,000 solutions can be titrated; it is unaffected by carbon dioxide, and phosphoric acid can be titrated as a monobasic acid. It is available for the titration of feeble bases such as the alkaloids.

Lacmoid (Resorcin Blue).—This substance owes its distinctive properties to *lacmosol*, which can be isolated from the commercial product and purified, this pure product being superior to the ordinary material. A 0·3% alcoholic solution is employed, but a better colour change is obtained if 5 g. of naphthol green are dissolved in a litre of this solution. Although the colour changes resemble those of litmus, the indicator bears a closer resemblance to methyl red. It is only slightly affected by carbon dioxide, although direct titration of carbonates is not satisfactory in cold solution; it is useless for organic acids.

Litmus.—This occurs in commerce in the form of small cubes mixed with a large proportion of calcium carbonate. An aqueous extract of this substance contains free alkali and also a variable proportion of colouring matters which vitiate the delicacy of the reaction, and it is better to use the specially prepared solutions which are available commercially; they must be kept in vessels to which the air has free access, for if kept in closed vessels they undergo fermentation and become decolorised. The colour of the solution should be purple; it is affected by carbon dioxide, sulphur dioxide, and hydrogen sulphide.

The colour change is rendered more delicate by conducting the titration in monochromatic sodium light: the red solution then seems colourless, and the blue solution almost black. Litmus is not well adapted for use in ordinary artificial light.

Methyl Orange (Helianthin, Poirrier's Orange III).—This substance, prepared by diazotising sulphanilic acid and coupling it with dimethylaniline, was introduced as an indicator by Lunge in 1878. 1 g. of the pure sodium salt or free acid is dissolved in one litre of water, and one or two drops of this solution are used in each titration; the colour change is sharper if the solution is only extremely faintly coloured. The great advantage of methyl orange lies in the fact that it is unaffected by very weak acids, so that, for example, carbonates, borates, and sulphides may be titrated even in cold solution as if they were the free base. It is necessary to use this indicator in the cold, since its changes are not sharp in hot solution. Also, since it is not so sensitive as many indicators, the solution to be titrated should preferably not be more dilute than N/5. With N/10 solutions, especially when carbonates are being titrated there is a distinct brownish transition tint, and results may be uncertain to within about 0·05 c.c. Methyl orange must not be used in the presence of nitrous acid, which destroys it.

Hickman and Linstead (J.C.S. 1922, 121, 2502) found that the colour change could be made sharper, and also more readily visible in artificial light, by adding xylene cyanol FF (1·4 g. to 1 g. of methyl orange in 500 c.c. of 50% alcohol), which acts as a "screen." The colour change is then magenta→grey (at p_H3·8)→green.

Methyl Red.—This indicator, analogous to methyl orange but with anthranilic acid replacing sulphanilic acid, was introduced by Rupp and Loose in 1908. A 0·2% alcoholic solution is employed, two drops being used in each titration. The colour change is very pronounced, and weak bases may be titrated in $N/100$ solution. Sodium hydroxide solutions containing only traces of carbonates can be titrated with the aid of methyl red, but larger amounts of carbonate render the end-point indefinite, so when methyl red is used in the titration of carbonates, the solution must be boiled after each addition of the acid when the end-point is being approached.

p-*Nitrophenol*.—This may be employed in aqueous solution; it has the advantage that its range extends up to the point of theoretical neutrality, and, moreover, it is less affected by proteins than are some other indicators. On the other hand, its colour is not very intense.

Phenacetolin.—1 g. is dissolved in 500 c.c. of alcohol. It is yellow at p_H 0–3, brown-red at p_H 5, pink at p_H 6–10 (*i.e.* with carbonates of the alkalis), and almost colourless at p_H12 (*i.e.* with caustic alkalis). It is used, therefore, for estimating both hydroxide and carbonate when present in the same solution.

Phenolphthalein.—This was proposed as an indicator by Luck (Z. anal. Chem. 1877, **16**, 322); one or two drops of a 0·5% alcoholic solution are used in each titration. It is very useful for titrating organic acids, but is useless in the presence of ammonium salts or of carbonic or hydrogen sulphide (*see* p. 638).

Rosolic Acid (*aurin, corallin*).—This is used as a 1% solution in 60% alcohol, a few drops sufficing for 100 c.c. of liquid. It is affected by carbonates and sulphides, but records the neutralisation of sulphurous acid by ammonia at the $(NH_4)_2SO_3$ stage. It has the advantage that it can be employed in 50% alcoholic solutions.

Thymolphthalein.—This resembles phenolphthalein, but its different colour change and slightly different range sometimes make it preferable.

Tropæolin-O.—Although its high range limits the applicability of this indicator, yet it has been used by Prideaux (Z. anorg. Chem. 1913, 83, 362) for the direct titration of boric acid by alkali; 10–20 drops of 0·04% solution are used, and the boric acid solution should be saturated with sodium chloride.

Mixed Indicators.—A mixture of two indicators will often give a sharper colour change than either indicator separately, and by suitable choice of indicators it is possible to obtain a sharp change over a narrow range of p_H, and thus to secure an accurate titration which might otherwise be difficult; *e.g.* the titration of carbonate to the bicarbonate stage, for which Simpson (Ind. Eng. Chem. 1924, **16**, 709) uses 6 parts of thymol blue to 1 part of cresol red and titrates from the purple-violet through blue to a rose colour. A list of 25 such mixed indicators with their characteristics is given by Kolthoff (Biochem. Z. 1927, **189**, 26; *see also* Kolthoff and Furman, *op. cit.*, and under *Methyl Orange*, above).

Preparation of Standard Acids and Alkalis

Standard solutions of acids and alkalis are usually prepared on the *normal* basis (*see* p. 636). In acidimetry and alkalimetry it is essential to have a solution of some acid or alkali, the concentration of which is known with great accuracy; this solution serves to standardise the others of its class, and if it is hydrochloric acid it may be used indirectly to standardise solutions of other classes (*e.g.* silver nitrate or potassium iodate). Various suggestions have been made for acid standards, but hydrochloric acid is the most generally useful, although sulphuric acid (or occasionally oxalic acid) is used.

The commonest method of determining the concentration of either of the two inorganic acids is to titrate it against weighed amounts of pure anhydrous sodium carbonate. Separate weighed quantities of the solid are dissolved in 50–100 c.c. of cold distilled water and titrated by the acid, methyl orange being the indicator. The concentration of the acid is calculated from each result, and the mean is taken as correct.

Chemically pure sodium carbonate, which should be free from all but minute traces of chloride and sulphate, is dried at 280°–300°C. in a platinum crucible with continual stirring. Alternatively, the bicarbonate may be heated to constant weight at the same temperature. Complete dehydration of the carbonate is said to be effected by washing it with alcohol and drying it at 110°C. (Ind. Eng. Chem. [Anal.], 1934, **6**, 336).

The foregoing method, although extensively used, has been adversely criticised, mainly on the ground that complete dehydration cannot be effected without slight loss of carbon dioxide; it is asserted that this occurs even at 170°C., but this statement has been disputed, and even now (1937) the stability of carbonate towards moderate heat is much discussed, some authors asserting that a temperature of 400°C. is safe.

A satisfactory method of checking the values obtained by the carbonate process depends on the fact that sodium oxalate is converted into the carbonate on ignition. As the oxalate can be prepared in a state of high purity, the residue of carbonate theoretically obtainable from a known weight of oxalate can be calculated, and the presence of any sodium oxide is immaterial if the calculation is based on the original weight of oxalate. The weighed oxalate is carefully heated in a platinum crucible until all the separated carbon has been burnt off and the residual carbonate begins to fuse; the cooled residue is dissolved in water and titrated as already described (Sörensen, Z. anal. Chem. 1905, **44**, 156).

From time to time many other solids have been proposed as standards; the following are noteworthy:

Potassium tetroxalate,

$$KHC_2O_4,H_2C_2O_4,2H_2O;$$

succinic acid; *borax* (Rimbach, Ber. 1893, **26**, 171), which has an equilibrium water vapour pressure close to that of laboratory air under ordinary conditions of temperature and

a measured volume of the acid is added to a weighed excess of sodium carbonate in a platinum dish, the solution evaporated, the residue dried at 300°C. and weighed. This method is preferable to gravimetric determination of the acid as barium sulphate.

Sulphuric acid solutions of definite concentration may be prepared by specific gravity measurements (Pickering, J.C.S. 1890, 57, 64). A quantity of the purest acid is diluted with half its volume of water, and the specific gravity of the solution accurately determined with a Sprengel pyknometer at 15° or 18°. The percentage of actual H_2SO_4 in the solution is then found by reference to tables giving the values for 15°/15° or 18°/18° (*see* Sutton's "Volumetric Analysis," 12th ed., 1935, p. 56). If the specific gravity at 15°/15° is not corrected to vacuum standard, the table given in J.S.C.I. 1902, 21, 1511, may be used, whereas the other tables have been so corrected. Between the limits of 66 and 81% the following equations reproduce the uncorrected values with an error not exceeding 0·04%:

$$P=86S_{15}-69{\cdot}00$$
$$P=86S_{18}-68{\cdot}82$$

where P=percentage of sulphuric acid, and S_{15} and S_{18} are the specific gravities at 15° and 18° respectively uncorrected for buoyancy (Marshall, J.S.C.I. 1899, 18, 4). The diluted acid may be kept in a stoppered bottle without change, and can be weighed out and further diluted as required.

Oxalic Acid.—A normal solution is prepared by dissolving 63·02 g. of the pure dihydrate, $H_2C_2O_4,2H_2O$, in water and diluting it to 1 litre. The crystals tend to lose water in a warm atmosphere, so the solution should be checked against a standard alkali with phenolphthalein as indicator, or against an accurately standardised potassium permanganate solution (*cf.* p. 646). Oxalic acid solutions are somewhat unstable and should be checked frequently.

Sodium Hydroxide.—To prepare a normal solution, clear transparent lumps of A.R. material are selected, any opaque portions of surface scraped off, and about 50 g. dissolved in a litre of distilled water. The cooled solution is standardised against *N*-hydrochloric acid with methyl orange as indicator.

For the preparation of sodium hydroxide solutions free from carbonate several processes are available: (i) an emulsion of freshly slaked lime is added to the solution, and after the solid has settled the clear liquid is decanted off; (ii) a solution of baryta is similarly used; (iii) sodium is suspended in a cage of silver wire above a basin of water in a large desiccator, and the drippings fall into the water, giving the required solution; (iv) addition of sodium sulphate to baryta solution; (v) a concentrated solution is prepared from equal weights of the base and water, and is decanted from the insoluble sodium carbonate which settles during several days' standing. Method (ii) has the disadvantage that the solution gives a precipitate with sulphuric acid or sulphates.

Potassium Hydroxide.—This is prepared analogously to sodium hydroxide, but if it is required free from carbonate, method (v) is not available since potassium carbonate is too soluble in the concentrated hydroxide solution.

These carbonate-free solutions may often be used instead of baryta solutions, but the same precautions have to be adopted in keeping them.

Barium Hydroxide.—40 g. of the crystalline hydroxide, $Ba(OH)_2,8H_2O$, are dissolved in about 600 c.c. of boiling water in a flask provided with a stopper carrying a siphon arrangement. When the solution has become cold, the excess baryta will have crystallised out and carried with it any suspended carbonate. The clear solution (about 0·4*N*) is siphoned off into about three times its volume of recently boiled and cooled distilled water, and the diluted solution is kept in an aspirator fitted with a soda-lime guard-tube, so that it can be run off through a tube fitted to the tubulure directly into a burette. The solution is standardised against succinic acid, phenolphthalein being used as indicator; or a measured volume may be evaporated to dryness with a slight excess of sulphuric acid, the residual barium sulphate being gently heated and weighed.

The chief use of this solution is in titrating organic acids, phenolphthalein being the indicator. Carbon dioxide must be excluded. Baryta kept in glass vessels may acquire traces of silica which affect its use for determination of carbon dioxide (Z. anal. Chem. 1933, 94, 1).

Ammonia.—Solutions of ammonia slowly lose the gas if they are more concentrated than *N*/2, but those of this or lower concentration are very stable. An approximately *N*/2-solution may be prepared by diluting 28 c.c. of the ordinary concentrated solution (sp.gr. 0·88) to 1 litre; it is standardised against hydrochloric acid with methyl red as indicator.

Expansion of Standard Solutions.—In order to correct for expansion or contraction of standard solutions with change of temperature, it is important to note that these deviations differ from those of water if the solution is not very dilute. The following table is taken from Schlösser's data (Chem.-Ztg. 1904, 28, 4; 1905, 29, 510) for correction to 15°C., the value given being the number of c.c. to be added to or subtracted from 1,000 c.c. at the given temperature.

Temp.	0·1*N*-Solutions.	*N*-HCl	*N*-H_2SO_4	*N*-Oxalic acid.	*N*-NaOH
5°	+0·60	+1·26	+1·94	+1·33	+2·18
10°	+0·46	+0·76	+1·09	+0·81	+1·18
15°	±0·00	±0·00	±0·00	±0·00	±0·00
20°	−0·76	−0·97	−1·30	−1·05	−1·33
25°	−1·79	−2·14	−2·76	−2·34	−2·85

Typical Acidimetric and Alkalimetric Estimations.

Determination of Total Alkali.—About 10 g of the substance are dissolved in water, filtered if necessary, and the solution diluted to 500 c.c.; 50 c.c. are withdrawn, and titrated with N-hydrochloric acid, methyl orange being used as indicator. *If the substance is difficultly soluble* in water, 1 g is boiled with a measured excess of the acid, and the excess is titrated with standard alkali after being cooled. The result gives the volume of acid required to neutralise the total alkali, *i.e.* that present as hydroxide, carbonate, bicarbonate, sulphide, sulphite, thiosulphate, aluminate, and silicate.

Alkaline Hydroxide in Presence of Carbonate.—100 c.c. of the above solution are heated, mixed with excess of barium chloride solution, cooled, diluted to 250 c.c., and well shaken. When the precipitate has settled, 50 c.c. of the clear liquid are withdrawn and titrated with standard acid. The hydroxide thus determined is one-twenty fifth of that in the original substance. The carbonate is precipitated as insoluble barium salt, and the hydroxide content is unaffected.

$$xM_2CO_3+yMOH+xBaCl_2 = xBaCO_3+yMOH+2xMCl$$

The solution cannot be filtered, since the alkali would absorb carbon dioxide from the air, causing more carbonate to be precipitated owing to reaction with the excess barium chloride. A considerable excess of barium chloride is necessary to repress the slight solubility of the barium carbonate.

In order to avoid the slight error due to the volume of the precipitate, and to economise time, Watson Smith (J.S.C.I. 1882, **1**, 85) adds just sufficient barium chloride to precipitate the carbonate. According to him, no barium carbonate remains in solution, and even if carbon dioxide is absorbed, there is no excess barium to precipitate it, so no alkali is lost. The barium chloride is added gradually to the *hot* solution until precipitation is just complete, and *the solution is filtered into a 250 c.c. flask*, an aliquot portion being titrated. Sörensen and Andersen (Z. anal. Chem. 1908, **47**, 279) state that hydroxide or bicarbonate should be converted into neutral chloride or normal carbonate, by acid or alkali respectively, in order that pure $BaCO_3$ may be precipitated. Alternatively, the whole of the liquid containing the barium carbonate in suspension may be titrated with oxalic acid, with phenolphthalein as indicator, since this is not affected by the barium carbonate.

Carbonates in the Presence of Hydroxide.—The solution is coloured very faintly yellow with phenacetolin, and titrated with standard acid until the colour changes to a rose tint. The acid thus added corresponds to the free hydroxide present. Further addition of acid now causes an intensification of the red colour, but later this becomes yellowish and finally a golden yellow. The additional acid thus added corresponds to the carbonate present (Lunge, J.S.C.I. 1882, **1**, 56). This method is not accurate for small proportions of hydroxide in presence of large quantities of carbonate.

The following method (Warder, Chem. News, 1881, **43**, 228) gives fairly satisfactory results, especially for relatively small quantities of carbonate. To the cold solution, preferably at 0°C. and saturated with sodium chloride, phenolphthalein is added, and standard hydrochloric acid is run in slowly, the burette tip being immersed in the liquid, till the indicator becomes colourless. At this stage (x c.c. of acid) all the hydroxide and half the carbonate have been neutralised. Titration is now continued with addition of methyl orange until this indicator shows a pink tinge (y c.c. more of acid). Therefore the carbonate is equivalent to $2y$ c.c., and the hydroxide to $(x-y)$ c.c. Simpson's indicator (*see* p. 641) is available for the first stage.

Evans (Analyst, 1937, **62**, 122) gives a method *for determination of carbonate, hydroxide, and cyanide* (as in plating-baths), and describes a useful apparatus for the precipitation, filtration and washing of barium carbonate in absence of carbon dioxide.

To determine the proportion of lime in a mixture with chalk, 5 g. of the finely powdered substance are moistened with 10 c.c. of neutral alcohol and mixed with 490 c.c. of 10% sucrose solution (neutralised if necessary). After being shaken for 4 hours, the solution is filtered through a dry paper, and 50 c.c. are titrated by $N/2$ hydrochloric acid, phenolphthalein being the indicator.

Mixed Normal and Acid Carbonates.—The cold dilute solution is titrated in presence of phenolphthalein, with the burette tip under the liquid, and the disappearance of colour corresponds to the conversion of all the carbonate into bicarbonate. The liquid is then boiled and titration is continued until the solution remains colourless after prolonged boiling. If x c.c. are added up to the first stage, and y c.c. in all, then $2x$ c.c. represents the normal carbonate, and $(y-2x)$ c.c. the bicarbonate. As before, better results are obtained if considerable sodium chloride is added to the solution to be titrated. Also, thymol blue gives a better indication of the first stage, titration being carried only to a green tint.

Titration of carbonate to the bicarbonate stage may be effected by use of Simpson's mixed indicator (*see* p. 641), but in all cases it is best to use a comparison solution containing the anticipated amount of sodium bicarbonate and the same amount of indicator in the same volume of liquid as in the test solution.

Lunge used a different method, based on the reaction:

$$xM_2CO_3+yMHCO_3+zNH_3+(x+y)BaCl_2 = (2x+y)MCl+yNH_4Cl+(x+y)BaCO_3 +(z-y)NH_3$$

The solution to be tested is mixed with a measured excess of $N/2$-ammonia, excess of barium chloride added, and the liquid diluted with recently boiled water to a definite volume. When the precipitate has settled, a portion of the clear liquid is withdrawn by a pipette and titrated for excess ammonia by standard acid. The difference between the ammonia added and that found finally corresponds to the bicarbonate present.

Another method is to add a definite excess of carbonate-free sodium hydroxide, the resulting mixture of hydroxide and carbonate being analysed as above.

None of these methods is very accurate if the proportion of normal to acid carbonate is small.

Ammonia.—Free ammonia in its aqueous solution is determined by weighing 10 c.c. in a light, stoppered, graduated, tared flask, and titrating it with standard acid and methyl red. The weighing gives both the weight taken for analysis and the specific gravity.

Combined ammonia is determined by boiling the substance with a considerable excess of sodium hydroxide solution, absorbing the ammonia in a measured excess of standard acid, and titrating this excess by alkali. The ammonia is most efficiently removed by a current of steam. If organic nitrogen compounds are present, these yield some ammonia on distillation with caustic alkali but not with magnesia, so a suspension of the latter should be used. Winkler prefers to absorb the ammonia in 2% boric acid solution and titrate it directly with methyl red or methyl orange as indicator, since this acid does not affect these indicators.

Ronchèse (J. Pharm. Chim. 1907, 25, 611) and Wilkie (J.S.C.I. 1910, 29, 6) determine ammonia in its neutral salts by adding a large excess of formalin (5 c.c. usually suffice) which has been neutralised to phenolphthalein, and after one minute titrating the acid which has been liberated owing to removal of the ammonia to form hexamethylenetetramine. If the salt solution is not neutral initially, it may be neutralised with methyl orange or methyl red as indicator, phenolphthalein being inadmissible at this stage; if an acidity is due to a weak acid, neutral red should be used instead of the other indicators.

Hydrochloric, Hydrobromic, Hydriodic, Sulphuric, and Nitric Acids.—These acids are determined by direct titration with standard alkali, using methyl orange, methyl red, or bromophenol blue as indicator.

Oxalic, Tartaric, Citric, Acetic, and Lactic Acids.—These acids may be similarly determined if phenolphthalein is used as indicator. Oxalic acid may be titrated with litmus as indicator if the solution is boiled. Methyl orange can be used if the oxalic acid is first nearly neutralised and then treated with excess of neutral calcium chloride solution, the titration being virtually that of hydrochloric acid liberated by double decomposition; if the chloride is added before the acid is nearly neutralised, the calcium oxalate carries down some acid, and the results are erroneous.

Boric Acid.—This cannot be directly titrated as an acid, since it is too weak to give accurate results with any of the ordinary indicators (*see* p. 639), and borates titrate as if they were the free base. If, however, the solution contains at least 30% of its weight of glycerol, the complex glyceroboric acid can be titrated in presence of phenolphthalein, the boric acid being virtually monobasic (Thomson, J.S.C.I. 1893, 12, 432). Addition of 5–10% of mannitol to the solution has a similar effect (Jones, Amer. J. Sci. 1899, 7, 847). In the presence of phenolphthalein, the absence of carbonates must be ensured.

Sulphurous Acid.—This acid can be titrated directly by sodium or potassium hydroxide (not by ammonia) if methyl orange, phenolphthalein, or rosolic acid is used as indicator. The first indicator denotes the stage $MHSO_3$ and the other two show the M_2SO_3 stage. By utilising this fact it is possible to determine both sulphite and bisulphite together.

Phosphoric and Arsenic Acids.—These are monobasic with methyl orange or, better, bromocresol green, and dibasic with phenolphthalein or, preferably, thymolphthalein. For the second stage, a mixture of phenolphthalein with two parts of α-naphtholphthalein gives a sharp and accurate end-point. These acids can be titrated with baryta and phenolphthalein; towards the end of the reaction time must be allowed for the gelatinous $Ba_3(PO_4)_2$ to change into the crystalline $BaHPO_4$. Advantage may be taken of the different basicity as indicated by the above methods to estimate phosphoric acid in presence of monobasic acids such as hydrochloric acid.

Segalle (Z. anal. Chem. 1895, 34, 33) precipitates phosphoric acid as $MgNH_4PO_4$ by addition, first, of a known volume of standard ammonia, and then of magnesium sulphate, and the excess of ammonia in an aliquot part of the filtered solution is titrated by standard acid with methyl red as indicator; or the precipitate may be filtered off, washed with ammonia and then with 50% alcohol, and dissolved in excess of standard acid, the excess being titrated by standard alkali (Stolba). Both these methods are equally applicable to arsenic acid. The efficient washing of the precipitate by alcohol is difficult to achieve.

Wilkie (J.S.C.I. 1909, 28, 68) adds to the acid solution excess of silver nitrate followed by excess of sodium acetate, whereby Ag_3PO_4 is precipitated and the corresponding amount of acetic acid (3 equivs.) is liberated and can be titrated as usual. A recent improvement (Simmich, Angew. Chem. 1935, 48, 566) is to neutralise the solution to methyl orange, add not more than 3·5 equivs. of silver nitrate, and titrate, by using bromothymol blue, the nitric acid liberated according to the equation, *e.g.*:

$$KH_2PO_4+3AgNO_3 = Ag_3PO_4+KNO_3+2HNO_3$$

Free phosphoric acid can be titrated as a tribasic acid if calcium chloride is added to the solution in the ratio of 5–10 mols. per mol. of H_3PO_4, so as to avoid formation of $CaHPO_4$ (Bull. Soc. chim. 1933, [iv], 53, 963).

Carbonic Acid.—In solution, this acid is determined by adding excess of ammonia and calcium chloride. The liquid is then boiled, and the precipitated calcium carbonate collected, well washed, and dissolved in a measured excess of standard hydrochloric acid, the excess being titrated by standard alkali to methyl orange:

$$CO_2=0{\cdot}022\times \text{vol. of } N\text{-acid consumed.}$$

Insoluble carbonates are weighed into a flask carrying a cork fitted with a bulb and delivery tube. The bulb contains 40% phosphoric acid,

which is allowed to drop slowly on to the carbonate, and the evolved gas is led into a flask containing fairly strong ammonia. The second flask is closed with a cork through which pass the delivery tube, which should end just above the surface of the ammonia, and a guard tube filled with pieces of glass moistened with ammonia. Finally when all the gas has been expelled, by moderate heating if necessary, the CO_2 *in the ammonia is determined by means of* calcium chloride as above (Gooch and Phelps, Amer. J. Sci. 1895, 50, 101, who, however, used hydrochloric instead of phosphoric acid). The process can be adapted to the determination of CO_2 in mineral waters

Seyler (Analyst, 1897, 22, 312) discusses the occurrence of carbon dioxide, free and combined, in natural waters.

Hydrofluoric Acid—This may be accurately titrated by carbonate free potassium hydroxide and phenolphthalein, but if it contains silicofluoric acid, this is titrated as a dibasic acid and the end point fades slowly owing to the reaction *of* K_2SiF_6 *with the excess alkali (see below)*

Silicofluoric Acid.—Solutions of this acid should be diluted with an equal volume of alcohol and titrated as above; *the* K_2SiF_6 is insoluble in the alcoholic solution and does not undergo the further reaction mentioned above Alternatively, this salt may be filtered off and further titrated

$$K_2SiF_6+4KOH=6KF+SiO_2+2H_2O.$$

Combined Acids in Salts may be roughly determined by adding to the salt solution a measured excess of sodium hydroxide or carbonate, boiling the mixture, letting the *precipitate settle, and titrating the excess* alkali in an aliquot part of the liquid, methyl orange being the indicator. The volume of *alkali* consumed is a measure of the combined acid. For salts of copper, silver, mercury, cobalt, nickel, iron, and chromium, the hydroxide should be used, for those of calcium, barium, strontium, magnesium, aluminium, zinc, bismuth, and manganese, the carbonate should *be used.*

For strongly coloured solutions or salts which are readily hydrolysed, Kiefer's method (Annalen, 1855, 93, 386) is still sometimes used: 60 g. of copper sulphate are dissolved in water, and ammonia is added until nearly all the precipitate has redissolved. The solution is diluted to 900 c.c., allowed to settle, and the *clear liquid filtered through* glass wool and diluted to a litre. When this liquid is gradually added to an acid solution observed against a black background, a temporary precipitate is redissolved until all the free acid is neutralised, but then remains permanent. A blank is similarly standardised on 10 c.c. of *N*-sulphuric acid. The results vary with conditions of concentration, etc. The nitrate is used instead of the sulphate if barium, etc., is present. The solution requires frequent standardisation.

Free Acid in Salts may be determined by adding glycerol to the solution and titrating the acid (Wagner, Z. anal. Chem. 1933, 95, 311). *The glycerol forms a complex with the metal and* the salt is not then subject to hydrolysis. Free acid in iron or aluminium sulphate may be determined by adding 10 g. of sodium chloride and 5 g of sodium fluoride and titrating without removal of the colourless precipitated fluoride, phenolphthalein being the indicator.

For titration of free acid in iron or copper salts, *see* Ahlum (Proc. Chem. Soc. 1906, 22, 63) and Sims (Chem. News, 1907, 95, 253) respectively.

Bibliography.—Sutton's "Volumetric Analysis," *12th ed, 1935; Treadwell,* "Analytical Chemistry," vol. 2, 8th ed. (trans by Hall), 1935, Lunge's "Technical Chemist's Handbook," 3rd ed. (Cumming), *1929*; Kolthoff and Furman, "Volumetric Analysis," 1929.

OTHER VOLUMETRIC PROCESSES.

Preparation of Standard Solutions.

POTASSIUM PERMANGANATE.—This is employed as an oxidising agent, usually in dilute sulphuric acid solution, when it reacts according to the equation:

$$2KMnO_4+4H_2SO_4 \\ =2KHSO_4+2MnSO_4+3H_2O+5O$$

The oxidation of ferrous sulphate, for example, is represented thus

$$2KMnO_4+10FeSO_4+9H_2SO_4 \\ =2KHSO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O$$

It is sometimes simpler to regard the process as occurring between oxides

$$10FeO+Mn_2O_7=5Fe_2O_3+2MnO.$$

or as a transfer of electrons from ferrous ions:

$$5Fe^{\cdot\cdot}+MnO_4'+8H^{\cdot}=5Fe^{\cdot\cdot\cdot}+Mn^{\cdot\cdot}+4H_2O$$

The utility of permanganate depends on the *facts that such oxidations are rapid and quantitative*, and that its strong colour enables it to act as its own indicator, the smallest excess being readily detected. Most oxidations occur at the ordinary temperature, but that of oxalic acid requires a temperature of 60°–80°. It is essential to have a moderate excess of sulphuric acid present (say, 2–5 c.c. of concentrated acid per 100 c.c. of solution), for otherwise manganic *hydroxides may separate and spoil the titration.* The presence of hydrochloric acid should be avoided if possible, since it tends to react with the permanganate, particularly in presence of iron salts. The resultant error can be minimised by *certain devices described under* IRON. The addition of colloidal silicic acid, in the form of 5 c.c. of a solution of water-glass (sp gr. 1·17), was claimed to obviate this *source of* error (Analyst, 1909, 34, 306), but this has been disputed (Chem. Ztg. 1919, 43, 51; 1920, 44, 310, 682; Z. anal. Chem. *1923, 62, 417*).

Preparation and Titration of the Solution—An *N*/10 solution (3·16 g. per litre) is most convenient for general use. After being prepared, the solution should be set aside for a few days, then filtered from any deposited dioxide (which catalyses its decomposition) through a sintered-glass filter, and standardised. It is then fairly stable for long periods if stored out of bright light and protected from dust. The solution is best standardised against sodium oxalate.

Titration against Sodium Oxalate.—This substance was suggested as a standard by Sörensen,

and is generally regarded as the best for the purpose as it can be obtained very pure and anhydrous. It should be dried at 100°C. for few hours before use. The following method (McBride, J. Amer. Chem. Soc. 1912, 34, 393) had been regarded for many years as the best, but has recently been criticised (*see below*).

Three or four portions of the pure dry oxalate (0·25–0·30 g.) are separately dissolved in 200–250 c.c. of water containing 5 c.c. of concentrated sulphuric acid, heated to 80°–90°C., and titrated, *with vigorous stirring* and *very slowly*, especially towards the end, until a faint permanent pink coloration is obtained. The final temperature should not be below 60°.

Fowler and Bright (J. Res. Nat. Bur. Stand. 1935, 15, 493) find that this method is apt to give high results for the permanganate factor; they recommend that 90–95% of the volume of permanganate expected to be required be added to the acid oxalate solution at 25°–30°, the titration being then completed after the solution has been warmed to 55°–60°.

Other common methods for the standardisation are against: oxalic acid dihydrate, $H_2C_2O_4,2H_2O$; ammonium oxalate,

$$(NH_4)_2C_2O_4,H_2O;$$

and Mohr's salt, $FeSO_4,(NH_4)_2SO_4,6H_2O$. The former practice of standardisation against iron wire should be discarded, since the traces of oxidisable impurities consume more permanganate than their own weight of iron, and correction for the actual iron content increases the error. Metallic iron produced by the decomposition of the pentacarbonyl, $Fe(CO)_5$, is, however, sufficiently pure for standardisation purposes (Z. anal. Chem. 1933, 91, 341); and the ferrous salt produced by dissolving pure silver foil in excess of acidified ferric alum solution in a current of carbon dioxide has been recommended for standardisation, especially if phosphoric acid is added to diminish the colour of the ferric salt (Z. anorg. Chem. 1924, 136, 193).

It is often convenient to express the concentration of a permanganate solution in terms of the weight of iron it can oxidise; thus 1 c.c. of N/10-permanganate=0·005584 g. of iron.

Potassium Dichromate.—A solution of this salt may replace permanganate in the titration of ferrous iron, with the advantage that it is not affected by dilute hydrochloric acid. An excess of mineral acid is essential. The oxidation may be expressed by any of the equations:

$$K_2Cr_2O_7+6FeCl_2+14HCl$$
$$=2KCl+2CrCl_3+6FeCl_3+7H_2O,$$
$$2CrO_3+6FeO=Cr_2O_3+3Fe_2O_3,$$
$$6Fe^{\cdot\cdot}+Cr_2O_7''+14H^{\cdot}=6Fe^{\cdot\cdot\cdot}+2Cr^{\cdot\cdot\cdot}+7H_2O$$

An N/10 solution is prepared by dissolving 4·904 g. of the pure dry salt in distilled water and diluting to 1 litre. The titrations are made at room temperature, but since the green colour of the chromic salt masks the colour of the excess of dichromate it is necessary to use either (i) an external indicator or (ii) an intensely coloured internal indicator.

(i) Drops of a very dilute solution of potassium ferricyanide solution, prepared by washing a small crystal repeatedly to free it from ferrocyanide and then dissolving it to give a very pale yellow solution, are placed on a white plate, and from time to time the end of a glass rod, previously dipped into the solution being titrated, is brought into contact with a drop of ferricyanide. As long as ferrous salt is present in appreciable amount a strong blue colour is obtained, but as the quantity diminishes, the colour becomes paler, then greenish-blue, until finally a drop ceases to give any colour; at this stage *about half a minute should be allowed for* any potential colour to develop. If the ferricyanide is too strong the end-point has a brownish tint.

(ii) It is more convenient to use an internal indicator, of which a variety is available. In conjunction with some of these it is necessary to add 2·5 c.c. of syrupy phosphoric acid (or its equivalent), and in any case a fairly high concentration of acid should be maintained by addition of 10 c.c. of concentrated sulphuric acid per 150 c.c. of liquid. A few drops of a 1% solution of diphenylamine in concentrated sulphuric acid, or, better, three drops of a 0·3% aqueous solution of barium diphenylamine-sulphonate are used as indicator, the end-point being marked by the persistence of an intensely blue-violet or a bright reddish-pink colour respectively. Another indicator of this type is tri-*o*-phenanthrolinoferrous sulphate,

$$[Fe(C_{12}H_8N_2)_3]SO_4,$$

which is readily prepared from 12 g. of the hydrated base and the equivalent of acid-free ferrous sulphate per litre; one drop of this M/50 solution usually suffices; the colour change is from an intense red to a pale blue, and *phosphoric acid is not required* (Walden, Hammett and Chapman, J. Amer. Chem. Soc. 1931, 53, 3908; 1933, 55, 2649). Numerous other indicators have been suggested; a few drops of a 1% solution of brucine in dilute sulphuric acid are effective if the acidity is kept above 3N-: the solution acquires a bright cherry-red colour at the end-point, and, as in the foregoing cases, except that of diphenylamine, mercuric and stannic salts do not interfere. Further, phenylanthranilic acid may be used under similar conditions to the phenanthroline compound (J. Amer. Chem. Soc. 1936, 58, 928). The colour change of diphenylamine is not evident in artificial light.

Ceric Sulphate.—This oxidising agent has the advantage over potassium permanganate, which it otherwise resembles, that its action involves only one step in valency instead of five:

$$Ce^{IV}\rightarrow Ce^{III}\ (cf.\ Mn^{VII}\rightarrow Mn^{II}),$$

and that the presence of hydrochloric acid is not inconvenient; on the other hand, its colour (orange) is not so intense as that of permanganate, and it cannot so readily serve as its own indicator. The solution is prepared by heating 50 g. of the commercial oxide (of which the oxidising power is equivalent to about 40% of CeO_2) or 50 g. of ceric nitrate with concentrated sulphuric acid—in the latter case, until all nitrous fumes are expelled—and

extracting the cooled mass with water to give a litre of solution, which should then be rather stronger than $N/10$, and be $N/2$ to N with regard to sulphuric acid. Alternatively, 35 g of purified cerous oxalate may be converted into oxide by heating at 600°C. in an iron crucible, and the oxide is then treated as above.

The solution is standardised on sodium oxalate in acid solution at 70°C, being added until a pale yellow colour due to ceric salt just persists

$$H_2C_2O_4 + 2Ce(SO_4)_2 = Ce_2(SO_4)_3 + H_2SO_4 + 2CO_2$$

It may also be standardised upon ferrous ammonium sulphate, titration being carried out at room temperature with 0 5 c c. of 0 1% aqueous solution of xylene cyanol FF as indicator, the colour changes sharply from green to orange and is readily reversible Methyl red (Furman and Evans, J Amer Chem. Soc 1928, 50, 755, 1675, 1930, 52, 2347) or erioglaucin A may be used as indicator; in the former case it is better to titrate in the reverse direction, and the ferrous solution is run in until the ceric solution is pale yellow, then the indicator is added together with sulphuric and phosphoric acids, and the titration is continued until the solution becomes violet. Erio glaucin A is yellow with ferric and rose with ceric solutions

Potassium ferrocyanide serves as a standard if a drop of diphenylamine solution (*see* p. 647) is used as indicator, or a drop of ferric chloride solution may be used instead, titration being carried out with vigorous shaking until the Prussian blue colour disappears Iodine (Swift, J. Amer Chem Soc. 1930, 52, 899) and arsenious oxide (Willard and Young, *ibid.* 1928, 50, 1372) have also been used for the standardisation.

Iodine, Sodium Thiosulphate, and Sodium Arsenite —$N/10$ solutions of these reagents are frequently used in conjunction with one another. The fundamental reaction between the first two is

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI,$$

although in certain circumstances oxidation to sulphate may occur to a small extent (Pickering, J C.S. 1880, 37, 128). In colourless solutions the colour of $N/10$ iodine suffices for it to act as its own indicator, but in coloured solutions or with weaker iodine it is necessary to use starch solution, which gives an intense blue colour with the least excess of iodine.

Starch Solution.—About 1 g. of powdered soluble starch is ground into a paste with a little cold water and slowly added to 200 c.c. of boiling water, the boiling is continued for a few minutes, and the solution cooled. It only keeps for a few days unless sterilised, and then, if kept in small bottles, completely filled and closed by rubber stoppers, it is stable over long periods. Addition of 1 mg. of mercuric iodide per 100 c.c. also preserves it.

Sensitiveness of the Iodine-Starch Reaction.—Starch must be used in cold solution, for heat greatly diminishes its sensitivity. Also, it must not be used in strongly acid solution, for if it is hydrolysed it ceases to give a strong, pure colour. Among other factors which affect the sensitiveness of starch, the concentration of soluble iodide is important, and this should be neither less than $N/150$ nor excessively high With only a very slight trace of iodine the colour is pink, but with more than a mere trace it is an intense blue.

In many titrations 1 c.c. of a 0 005% solution of methylene blue may replace starch (Analyst, 1910, 35, 309, 1912, 37, 252)

Iodine Solution —To 25 g. of potassium iodide, dissolved in a little water, 12 69 g. of pure iodine are added, the mixture shaken until dissolution is complete, and diluted to 1 litre. The solution should be kept in the dark and protected from dust. For direct preparation of small quantities of standard iodine, *see below.*

Sodium Thiosulphate Solution.—The degree of hydration of the crystals is not to be relied upon, so 25 g. are dissolved in a litre of water, and after standing out of direct sunlight for at least a week, the solution is standardised. It is fairly stable, and attempts to improve the stability by addition of borax ($M/100$) (Watson, J S C I. Victoria, 1932, 32, 679) are said to lead to inaccurate results (Hoikheimer, Pharm Ztg 1935, 80, 1330).

Sodium Arsenite Solution —4 946 g. of re-sublimed arsenious oxide are dissolved in a little warm pure sodium hydroxide solution, diluted to about 300 c c., made just acid to phenol phthalein by dilute sulphuric acid or a current of carbon dioxide, and mixed with 20 g of sodium bicarbonate in 500 c c. of water, the faintly acid reaction being restored by dilute sulphuric acid. The solution is then diluted to a litre; it is exactly decinormal, and keeps indefinitely.

A measured volume of the arsenite solution is titrated by the iodine solution, with addition of starch if necessary, and the iodine is thereby standardised. The reversible reaction

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI$$

proceeds completely to the right in neutral solution, and the excess of sodium bicarbonate secures this condition by neutralising the hydriodic acid produced. Owing to effervescence, due to the reaction between bicarbonate and hydriodic acid, the titration vessel should be covered except when the iodine is being introduced.

The thiosulphate solution is standardised on the iodine solution, or upon a solution prepared as follows. 0 5 g. of pure iodine, 0 1 g. of potassium iodide, and a trace of quicklime are ground together and heated on a sand-bath until iodine vapour is copiously evolved; the dish is then covered with a dry watch glass, and the greater part of the iodine sublimed on to it. The watch glass is then covered with a second accurately fitting glass and the pair are weighed, the weight of the glasses having been previously found. The whole is then carefully placed in 10 c.c. of a 10% aqueous solution of potassium iodide, and when the iodine has dissolved it is diluted to 100 c.c. and titrated by the thiosulphate.

The thiosulphate may also be standardised against permanganate which has been checked

on sodium oxalate: 1–2 g. of potassium iodide are dissolved in water, acidified with 5 c.c. of 2*N*-sulphuric acid, and 25 c.c. of *N*/10-permanganate added. The iodine liberated according to the equation

$$2KMnO_4+10KI+14H_2SO_4$$
$$=12KHSO_4+2MnSO_4+5I_2+8H_2O$$

is then titrated by the thiosulphate after dilution of the solution to 100 c.c.

Thiosulphate should not be standardised against a copper solution unless it is to be used for the titration of copper (*q.v.*), for the result is slightly in error with regard to other titrations. It may be standardised against pure potassium dichromate under the conditions prescribed under Chromium. The iodine liberated from a known weight of pure potassium iodate by potassium iodide in dilute acid solution also affords a good means whereby to standardise thiosulphate.

Titanous Chloride.—This reagent, introduced into volumetric analysis by Knecht (J. Soc. Dyers and Col. **19**, No. 6; Ber. 1907, **40**, 3819; Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," 1925), is a powerful reducing agent. For example, ferric chloride is rapidly and quantitatively reduced in cold hydrochloric acid solution, according to the equation

$$FeCl_3+TiCl_3=FeCl_2+TiCl_4,$$

and the end-point is reached when a red coloration disappears from 10–20 c.c. of 10% potassium thiocyanate solution which has been added to the ferric solution. Chromic acid and cupric salts may be similarly estimated, also many azo-dyes.

60 c.c. of commercial 15% titanous chloride (or sulphate) solution, which usually contains some iron, are mixed with an equal volume of concentrated hydrochloric acid, boiled for several minutes, and diluted to 1 litre with air-free water. The solution is stored in an atmosphere of hydrogen or carbon dioxide, and a convenient apparatus (*see, e.g.*, Sutton's "Volumetric Analysis," 12th ed., p. 262) is one in which the solution can be transferred from the storage aspirator to the burette without coming into contact with air or rubber.

The *solution* is standardised against an iron salt or potassium dichromate. (i) 35 g. of pure ferrous ammonium sulphate are dissolved in dilute sulphuric acid and diluted to 1 litre; 25 c.c. of this solution are then exactly oxidised by potassium permanganate, and the resulting ferric salt is titrated by titanous chloride as above. (ii) If dichromate is used, the thiocyanate indicator Jatar, J.S.C.I. 1908, *27*, 673, must be used externally by "spotting"; the colour changes, through orange to green and then violet, show the approach of the end-point, and the spotting need not be started until the green colour has just disappeared.

Ferric alum, purified as described by de Koninck (Bull. Soc. chim. Belg. 1909, 23, 222), may be used for the standardisation.

Stannous Chloride.—This reducing agent is more susceptible to atmospheric oxidation and change in titre than titanous chloride, but is occasionally used. Ferric salts are rapidly reduced in hot hydrochloric acid solution:

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4;$$

and iodine is reduced in cold acid solution:

$$2I_2+2SnCl_2=SnI_4+SnCl_4$$

10 g. of tin, preferable as pure foil, are dissolved in 200 c.c. of concentrated hydrochloric acid by boiling in contact with a piece of platinum foil, and the *solution is cooled, diluted to* 1 litre, and kept out of contact with air.

The solution may be standardised on iodine (*see under* Tin) or on a ferric solution, according to the purpose for which it is required. In the latter case, a known weight of pure ferrous ammonium sulphate is dissolved in water, hydrochloric acid added, and the iron oxidised by means of potassium chlorate, the excess chlorine being boiled off; the solution is cooled, diluted to 1 litre, and 25 c.c. used for titration. The solution to be titrated should be boiling and contain at least a quarter of its volume of concentrated hydrochloric acid, and the best method is to add a slight excess of stannous chloride, cool the solution, and titrate back with iodine. As far as possible, the process should be carried out in an atmosphere of carbon dioxide.

Silver Nitrate, Sodium Chloride, and Ammonium Thiocyanate.—These precipitation reagents are used for the determination of silver, copper, mercury, the halogen acids, cyanides and thiocyanates. They are usually made of decinormal concentration. *N*/10-silver nitrate is prepared from the pure dried salt and contains 16·99 g. per litre. If it is to be used in acid solution (*see* Volhard's process, below), it may be prepared by dissolving 10·788 g. of pure foil in a slight excess of nitric acid, boiling off nitrous fumes, cooling, and diluting to 1 litre. *N*/10-sodium chloride contains 5·845 g. of the pure dry salt per litre; it is used in Gay-Lussac's very exact method for the assay of silver (*see* Assaying). Neither ammonium nor potassium thiocyanate can be prepared accurately by direct weighing; 8 g. of the former or 10 g. of the latter are dissolved in water, the solution diluted to 1 litre, and 25 c.c. standardised against silver nitrate as described below.

Silver nitrate is used either in neutral or nitric acid solution. In the first case two types of indicator are available.

(i) Potassium chromate is used when halides are being estimated (Mohr's method). Silver chromate is decomposed by solutions of halides, forming the silver halide and metallic chromate; consequently, silver chromate cannot persist until all the halide has been precipitated. The first drop of silver nitrate in excess then produces a permanent precipitate of silver chromate, which gives a faint red tint to the previously pale yellow liquid, the change being more easily detected in *monochromatic sodium light*. Two drops of a 10% solution of potassium chromate are added to the solution, which should not be too dilute. Since silver chromate is soluble both in dilute acids and in ammonia, the solution must be neutral or very faintly alkaline with bicarbonate but not with ammonia. An acid solution should be neutralised with calcium

carbonate added in slight excess, and an alkaline solution should be barely acidified with dilute nitric acid and then treated as above. If barium is present, it should be precipitated by sodium sulphate, for otherwise it reacts with the chromate (the barium sulphate need not be removed).

(ii) Adsorption indicators may be used. If chloride is being titrated, 10 drops of a 0.1% aqueous solution of the sodium salt of fluorescein are added per 100 c.c. of liquid; as the silver solution is run in, with shaking, the suspension remains greenish-yellow until the first drop in excess is added, whereupon the precipitate assumes a pronounced reddish pink colour. The titrated solution should not be stronger than $N/20$ or weaker than $N/100$, and if acid, it should be treated with excess of sodium acetate. Dichlorofluorescein is serviceable for more dilute solutions (down to about $N/500$), and is preferable if acetic acid is present in more than very small amount.

For the titration of bromides, eosin (4 or 5 drops of 1% aqueous solution of sodium salt per 100 c.c.) is used, the colour of the precipitate changing to magenta at the end point, slight concentrations of nitric acid are not inimical, but in any case it is better to add excess of sodium acetate. Eosin is also available for the titration of iodides (preferably diluted to about $N/50$), but 1 c.c. of 1% dimethyldi-iodofluorescein is better. These indicators are preferable to potassium chromate for the titration of bromides and iodides, for this indicator is not very good with the former and is definitely erroneous with the latter.

In both types of titration, flocculation of the precipitate tends to obscure the end-point, and in order to minimise this, addition of a little 1% starch solution or of 5–10 c.c. of 0.1% chloride-free agar solution has been recommended.

In the presence of nitric acid, preferably not less than $N/2$, silver nitrate and ammonium or potassium thiocyanate are used in conjunction (Volhard, 1878). The addition of the thiocyanate to the silver solution precipitates white silver thiocyanate, and in presence of a ferric salt the completion of the precipitation is denoted by a red coloration due to ferric thiocyanate. The indicator is prepared by adding slightly diluted nitric acid, boiled free from nitrous gases, to a saturated solution of ferric alum until it is nearly colourless; 5–10 c.c. are used in each titration.

Determination of Individual Elements and Radicals.

Aluminium. (*a*) *Iodimetrically.* The neutral aluminium solution is treated with excess of potassium iodide and then with excess of potassium iodate; a measured excess of $N/10$-sodium thiosulphate is then added, and the whole is heated on the water-bath for 10 minutes. Aluminium hydroxide is precipitated according to the equation

$$2AlCl_3+5KI+KIO_3+3H_2O =2Al(OH)_3+6KCl+3I_2,$$

and the residual thiosulphate is titrated by $N/10$ iodine. The thiosulphate consumed is a measure of the acid originally combined with the aluminium and of any "residual acidity" due to extraneous acid already present. To determine the latter, excess of neutral potassium oxalate is added to another portion of the aluminium salt, which is thereby converted to a stable complex $K_3Al(C_2O_4)_3$, and the acidity is determined as before. The difference gives the acid stoichiometrically combined with the aluminium, and hence the amount of the metal itself may be calculated (Ber. 1925, 58, [B], 398).

(*b*) *By means of oxine* (8 *hydroxyquinoline*). The neutral or feebly acid aluminium solution (about 0.02 g. of Al) is diluted to 150 c.c., warmed to 50°–60°C., and treated with a moderate excess (sufficient to give a pronounced yellow colour) of a 2% solution of the reagent in $2N$ acetic acid to which ammonia has been added to produce a faint precipitate and which has been warmed to dissolve the latter. After addition of 40 g. of ammonium acetate in the minimum of water, the suspension is well stirred and allowed to cool to room temperature. The precipitate is collected on a sintered glass diaphragm (Jena G3), washed with hot water, and dissolved in concentrated hydrochloric acid. The oxine thus obtained from the precipitated $Al(C_9H_6ON)_3$ is then determined bromometrically, the reaction being essentially:

$$C_9H_7ON+2Br_2=C_9H_5ONBr_2+2HBr.$$

The acid solution is treated with a slight excess of $N/10$-potassium bromate bromide (2.784 g. $KBrO_3$ and 12 g. KBr per litre) as shown either (i) by "spotting" on to potassium iodide and starch paper or (ii) by a change from green to yellow produced in a few drops of added 1% indigo-carmine solution. After dilution of the solution and addition of a few c.c. of carbon disulphide (to avoid occlusion of iodine in the precipitate), a few c.c. of 10% potassium iodide are added and the iodine liberated, equivalent to the excess bromate, is titrated by $N/10$ thiosulphate, starch being used as indicator: 1 c.c. of $N/10$ $KBrO_3$ =0.2248 mg. of Al. For other details, *see* Z. anal. Chem. 1927, 71, 122, 369; 1929, 76, 135; J. Amer. Chem. Soc. 1928, 50, 1900; J. Res. Nat. Bur. Stand. 1935, 15, 87; Mitchell and Ward, "Modern Methods in Quantitative Chemical Analysis," 1932; Berg, "Das o Oxychinolin," Enke, 1935.

Separation of iron and aluminium can be effected by precipitating ferrous sulphide by means of hydrogen sulphide from ammoniacal tartrate solution, expelling hydrogen sulphide from the filtrates, and precipitating aluminium by oxine (Z. Pflanz. Dung. 1932, 26A, 1; Analyst, 1933, 58, 270).

Determination of aluminium in presence of iron, chromium, nickel, cobalt, copper and molybdenum involves their conversion into soluble complexes with tartaric acid and potassium cyanide, followed by precipitation of aluminium by oxine (Chem.-Ztg. 1934, 58, 1032). For the determination of aluminium by oxine in *nitriding steels*, *see* Bur. Stand. J. Res. 1933, 10, 327, and in *food*, *see* "Reports on Public Health and Medical Subjects, No. 78" (H.M. Stationery Office, 1935).

(*c*) A method recently suggested (Angew.

Chem. 1935, **48**, 589) is to precipitate aluminium as the arsenate, $AlAsO_4$, collect and wash this, dissolve it in hydrochloric acid, and determine the resultant arsenic acid (*q.v.*).

Antimony. ANTIMONIOUS SOLUTIONS. (*a*) Rochelle salt (1–2 g.) and an excess of sodium bicarbonate are added to the solution, which is then titrated with N/10-iodine. I_2=Sb (*v.* Arsenic).

(*b*) The hot hydrochloric acid solution (about $2N$ in acid and at about 80°C.) is titrated with N/10-potassium bromate, which has been standardised against pure antimony :

$$3SbCl_3+KBrO_3+6HCl =3SbCl_5+KBr+3H_2O$$

The end-point is shown by the bleaching of a few drops of methyl orange or methyl red added to the hot solution, a second titration being run with the indicator added only near the end (Z. anal. Chem. 1893, **32**, 415 ; Chem. News, 1907, **95**, 49).

(*c*) The solution (30 c.c.), containing tartaric acid (0·5 g.), concentrated sulphuric acid (5 c.c.), potassium bromide (0·2 g.), and 2 drops of a 0·5% solution of α-naphthaflavone, is titrated with N/10-potassium bromate until the faintly green opalescence changes to rust-brown ; the indicator colour-change is reversible (Z. anal. Chem. 1935, **102**, 111).

(*d*) The cold solution (200 c.c.), containing 10, 20, or 30 c.c. of concentrated sulphuric acid and 30, 15, or 10 c.c. respectively of concentrated hydrochloric acid, is titrated with N/10-permanganate, the end-point being taken when the colour persists for a few seconds (Z. angew. Chem. 1901, **14**, 1179 ; J. Amer. Chem. Soc. 1907, **29**, 66 ; J.C.S. 1933, 1).

(*e*) Ceric sulphate oxidises Sb^{III} quantitatively to Sb^V in approx. $6N$-hydrochloric acid solutions, with methyl red as indicator.

(*f*) Potassium iodate oxidises Sb^{III} in $5N$-hydrochloric acid as follows :

$$Sb_2O_3+KIO_3+2HCl =Sb_2O_5+ICl+KCl+H_2O ;$$

and a few c.c. of carbon tetrachloride are used to denote the end-point (*see* p. 658).

ANTIMONIC SOLUTIONS. (*a*) *By reduction* to the tervalent state, and estimation by one of the foregoing processes. Reduction may be accomplished : (i) by boiling the hydrochloric acid solution with sodium sulphite or sulphurous acid, preferably with the addition of 1 g. of potassium bromide (Ber. 1901, **34**, 1565) ; (ii) by boiling the sulphuric acid solution (100 c.c. containing 5 c.c. of concentrated acid and 4 g. of Rochelle salt) with 1·0–1·5 g. of potassium iodide till nearly all the iodine is expelled, exactly bleaching the remainder with dilute sulphurous acid, diluting, rapidly cooling, and neutralising. The solution is then titrated in bicarbonate solution with N/10-iodine (Amer. J. Sci. 1892, **42**, 213) ; (iii) the hydrochloric acid solution is shaken with mercury for 1 hour in an atmosphere of carbon dioxide ; As^V and Sn^{IV} are not reduced (Ind. Eng. Chem. [Anal.], 1933, **5**, 1).

(*b*) *Iodimetrically.*—The cold solution containing 20–25 c.c. of hydrochloric acid in a volume of 100 c.c. is mixed with at least a 5-fold excess of potassium iodide and the liberated iodine titrated with N/10-thiosulphate. I_2=Sb (Z. anorg. Chem. 1908, **58**, 202 ; *cf. ibid.* 1903, **37**, 337).

With increasing use in chemotherapy of organic antimonials, convenient methods of estimating antimony in such substances become important. The substance (0·05–0·07 g.) is digested with 2 g. of potassium sulphate and 3 c.c. of arsenic-free concentrated sulphuric acid in a loosely stoppered conical flask until the solution is colourless. After dilution with 25 c.c. of distilled water the solution is boiled for 3–5 minutes, 2–4 c.c. of concentrated hydrochloric acid added, and the solution rapidly cooled and diluted to 100 c.c. Of this solution 25 c.c. are rendered faintly alkaline to litmus by a 40% solution of sodium hydroxide, then acidified with 5 c.c. of 1% aqueous tartaric acid, and again rendered alkaline with 10 c.c. of a 4% solution of sodium bicarbonate. After adding 25–30 drops of 1% starch solution the antimony is estimated by titration with 0·01 N-iodine solution previously standardised against sodium antimony tartrate. By titration of the whole solution instead of an aliquot part, accurate results may be obtained with as little as 0·02 g. of substance (Indian J. Med. Res. 1929, **16**, 457).

The employment of organic antimonials as drugs in tropical diseases has led to the development of methods for estimating antimony both in the drugs themselves and in the excreta from patients. In the former case 0·2 g. of substance is mixed with 3 g. of potassium permanganate and treated with 15 c.c. of 50% sulphuric acid, and then gradually with 15 c.c. of concentrated sulphuric acid. The mixture is diluted with 15 c.c. of water, boiled for 5 minutes, and decolorised with a saturated solution of oxalic acid. After dilution to 120 c.c., 1 g. of urea and 2·5 g. of potassium iodide are added and the liberated iodine determined by thiosulphate after 15 minutes. Towards the end of the titration the liquid should be diluted considerably with water so as to destroy a yellow coloration not due to iodine which otherwise persists past the end point (J.C.S. 1926, 3181).

For separation of antimony from arsenic and tin, *see* p. 652.

For rapid determination of antimony in lead-rich alloys, *see* Analyst, 1937, **62**, 23.

Arsenic.—ARSENIOUS SOLUTIONS.—(*a*) *Iodimetrically.*—The solution, containing sodium bicarbonate in excess, is titrated with N/10-iodine as described under the standardisation of iodine solution. The bicarbonate may be replaced by disodium hydrogen phosphate (J. Amer. Chem. Soc. 1908, **30**, 31).

(*b*) *Oxidimetrically.*—(i) By titration with potassium bromate or potassium iodate, exactly as described under Antimony. (ii) In N/2-sulphuric acid, oxidation of arsenious acid solution (100 c.c.) is effected in the cold by N/10-potassium permanganate or ceric sulphate in presence of 3 drops of M/100-osmic acid as catalyst ; the titration is carried out slowly, and the indicator used is tri-o-phenanthrolino-ferrous sulphate, which is decolorised at the end-

point Iodine chloride can also be used as catalyst, or methylene-blue as indicator, provided the concentrations of acid are suitably adjusted (Z. anal. Chem. 1933, 95, 305; J. Amer. Chem. Soc. 1930, 52, 901; 1928, 50, 1372).

ARSENIC SOLUTIONS.—(*a*) *By reduction* to the tervalent condition and estimation as above. Reduction may be effected (i) by heating the sulphuric acid solution with sulphurous acid in a stoppered bottle for an hour, diluting and boiling to expel excess of sulphurous acid (Z anal Chem. 1883, 22, 378; Chem. News, 1886, 53, 221); (ii) with hydriodic acid as described under Antimony, but Rochelle salt is not required, (iii) by boiling the arsenate solution (0 25–0 5g in 20 c c), with 5 c.c. of concentrated acid, 2 c c of approximately $N/10$-iodine and 0 2 g. of red phosphorus until all iodine is expelled. Excess phosphorus is then filtered off from the solution containing tervalent arsenic (Analyst, 1933, 58, 469).

(*b*) *By Precipitation*.—The neutral or acetic acid solution is precipitated with excess of silver nitrate, the precipitated silver arsenate is collected, washed, dissolved in nitric acid, and the silver titrated by $N/10$ thiocyanate: $3Ag = As$.

(*c*) *Iodimetrically*.—The arsenate (0 5 g.) is shaken in a stoppered bottle with 30 c.c. of concentrated hydrochloric acid or $12N$ sulphuric acid and potassium iodide (0 5 g). After 15 minutes the liberated iodine is titrated by $N/10$-thiosulphate (Z. anal. Chem 1927, 70, 97).

ARSENIC IN ARSENICALS.—About 6 g of anhydrous sodium carbonate and 6 g. of sodium peroxide are mixed and about one third of the total is introduced into a nickel crucible, 0 2–0 25 g. of the finely powdered substance is added, mixed by a rotatory movement of the crucible and covered with the remainder of the fusion mixture. The crucible is heated cautiously at first and finally raised to a dull red heat for 5 minutes. The cooled mass is extracted with water into a 500 c c. conical flask, 25 c c. of sulphuric acid (1 : 1) are added, and the solution (250–300 c.c) boiled down to 100 c.c.; 1 g. of potassium iodide is added and boiling is continued to expel the iodine liberated. The pale yellow colour is destroyed by adding a drop of sulphurous acid. The solution is diluted to 100 c.c. with hot water, and arsenic precipitated as sulphide with hydrogen sulphide. The washed precipitate is dissolved off the filter paper into the original conical flask by 20 c c. of $N/2$ sodium hydroxide and washed through with hot water. The combined filtrates (250–300 c.c.) are treated with 30 c.c. of hydrogen peroxide (20 vol.), heated for 10 minutes on the steam bath to remove excess of the reagent, and after addition of a drop of phenolphthalein, acidified by adding 11 c.c. of sulphuric acid (1 : 1). The solution is again concentrated to 100 c.c. and treatment with potassium iodide is repeated. The resulting concentrate, after being decolorised with a drop of sulphurous acid, is diluted rapidly with water to 100 c.c., neutralised with $2N$-sodium hydroxide, and acidified with a drop of $2N$-sulphuric acid; 11% sodium phosphate, equal in volume to the $N/10$ iodine required in the titration, is added, and the arsenite solution is titrated with $N/10$ iodine (J.C.S. 1909, 95, 1477). The arsenical compound can also be oxidised by ammonium persulphate (*ibid.* 1925, 127, 1751).

SEPARATION OF ARSENIC, ANTIMONY AND TIN.—(i) Material containing these three elements is dissolved in nitric acid and the solution evaporated with sulphuric acid until copious fumes of the latter are evolved and all sulphur has distilled from the flask. To the cooled solution are added successively a few c c. of water containing 1·5 g. of recrystallised hydrazine sulphate, 80 c.c. of hydrochloric acid (sp gr. 1 19), and 1 g. of potassium bromide. Carbon dioxide is passed through the flask and the solution is distilled through a fractionating column 15–30 cm. long filled with broken glass; 80 c c. are collected in 40 minutes More hydrochloric acid (20–30 c c.) is added, and distillation continued until a further 20 c c. have been collected; the latter distillate is diluted and titrated with $N/10$ potassium bromate after addition of 1 g. of potassium bromide and 2 drops of methyl orange. If only a drop or two of bromate is required to discharge the colour, all the arsenic is in the first distillate, which is then titrated with bromate. The fractionating column is washed by filling with hydrochloric acid and the washings are used in the subsequent distillation of antimony from the residual liquid in the flask. For this purpose 7–14 c.c. of phosphoric acid (sp gr 1·7) are added to prevent distillation of tin. The flask is heated until the temperature of the liquid is 155°–165°, carbon dioxide is passed through, and hydrochloric acid is dropped into the liquid at the rate of 1 drop per second; the antimony should be removed in 40–50 minutes. The distillate is titrated with bromate as usual. To distil the tin from the residual liquid, the temperature is maintained at 140°, and a mixture of 1 part of hydrobromic acid (sp gr. 1·40) and 3 parts of hydrochloric acid (sp gr. 1·19) is slowly run in beneath the surface. Distillation is continued until a few drops of the distillate cease to react with hydrogen sulphide. The temperature should be kept below 145° to prevent bismuth from passing over. The distillate is diluted with an equal volume of water, and the tin reduced with *ferrum reductum* and titrated with iodine (Biltz, Z. anal. Chem. 1930, 81, 82; Scherrer, J. Res. Nat. Bur. Stand. 1936, 16, 253).

(ii) Separation is based on the different behaviour towards silver nitrate of arsenates and antimonates in ammoniacal fluoride solutions; the former are quantitatively precipitated as Ag_3AsO_4, but the latter do not react.

The substance (0 2 g), in a platinum dish, is dissolved in 20 c.c. of water, 5 c c. of conc. nitric acid, and 2–3 c.c. of hydrofluoric acid (48%). The resulting solution, after dilution to about 100 c.c. and neutralisation of most of the acid by ammonia, is covered with a quartz clock-glass, boiled gently, and 3 g. of potassium persulphate are added in small portions in order to oxidise Sb^{III} completely to Sb^{V}. The solution is diluted to 100 c.c. with water, and methyl orange added, followed by strong

ammonia drop by drop, until the liquid is golden. The solution is boiled, and the arsenic precipitated by addition of silver nitrate in slight excess while stirring vigorously with a rod of Pyrex glass until the precipitate has coagulated and settled completely. The clear supernatant liquid is tested with litmus paper, and dilute ammonia is added dropwise, if necessary, until the liquid is distinctly alkaline. After cooling, the silver arsenate is transferred to a sintered-glass crucible and washed first with a solution of ammonium nitrate (5 g./l.) and silver nitrate (0·25 g./l.), and then with a little alcohol. The precipitate is dissolved in nitric acid, and silver estimated by Volhard's method.

Excess of silver is removed from the filtrate with a minimum of dilute hydrochloric acid. The filtrate is poured into a quartz dish, treated with concentrated sulphuric acid (10–15 c.c.), and evaporated as far as possible on the water-bath; it is then heated for a few minutes to strong fuming over a free flame. Sulphur (2 g.) is added, the dish covered, and the liquid boiled gently for 20 minutes:

$$Sb_2O_5+2SO_2=Sb_2O_3+2SO_3$$

After cooling, a mixture of concentrated hydrochloric acid (20 c.c.) and water (80 c.c.) is added, sulphur is filtered off, the solution is diluted to 200 c.c., and antimony determined by titration with $N/10$-potassium bromate, standardised on pure antimony.

If arsenic, antimony, and tin are present together, for example as sulphides, the precipitate, in a small platinum or quartz dish, is dissolved in boiling concentrated sulphuric acid containing sulphur (2 g.). The solution is diluted, treated with hydrofluoric acid, and filtered from the sulphur. Arsenic and antimony are then precipitated by hydrogen sulphide, and separated as above; tin remains in solution, and is precipitated by ammonia, after expulsion of hydrofluoric acid (McCay, J. Amer. Chem. Soc. 1909, **31**, 373; 1928, **50**, 368).

Barium.—The barium solution is treated with carbonate-free ammonia, diluted to 100 c.c. and treated at 60°–70°C. with a slight excess of potassium chromate solution. The precipitated barium chromate is filtered off, thoroughly washed, and dissolved in a measured volume of standard acidified ferrous sulphate solution, the excess of which is determined by standard potassium permanganate. Calculation is based on the scheme $Ba \rightarrow BaCrO_4 \rightarrow H_2CrO_4=3$ equivalents Fe. Alternatively, the washed barium chromate is dissolved in $N/2$-hydrochloric acid, 2 g. of potassium iodide are added, and after a few minutes the liberated iodine is titrated.

Barium solutions may also be titrated directly into standardised sulphuric acid if a few drops of 0·2% aqueous sodium rhodizonate are added as indicator. The red colour changes at the end-point to yellow in neutral solution or colourless in acid solution. The titration is reversible only if the indicator is used externally (Analyst, 1933, **58**, 752). Addition of ammonium chloride improves the end-point (Z. anal. Chem. 1936, **105**, 346). Tetrahydroxyquinone has also been used as an indicator in this process (Ind. Eng. Chem. [Anal.], 1933, **5**, 403; 1936, **8**, 127).

Beryllium.—To the carefully neutralised beryllium solution, which does not contain metals yielding insoluble hydroxides, is added a known volume (excess) of $N/10$-hydrochloric acid, followed by potassium iodate and iodide in excess. The solution is swirled, sodium bicarbonate is added, and the liberated iodine is titrated by arsenious acid [Analyst, 1935, **60**, 291; *cf.* Aluminium (*a*) p. 650].

Bismuth.—(*a*) The metal is precipitated by shaking the bismuth solution during 20 minutes with aluminium powder (0·1 g.) and potassium hydroxide (7 g.); the solution is then boiled to dissolve the excess of aluminium. The bismuth is filtered off, washed with hot water, and added with its filter paper to 25 c.c. of $3N$-hydrochloric acid containing 3 g. of hydrated ferric chloride. After all the bismuth has dissolved, the ferrous iron ($3FeCl_3+Bi=3FeCl_2+BiCl_3$) is titrated by $N/10$-dichromate.

(*b*) Bismuth is precipitated by

$$[Cr(NH_3)_6](NO_3)_3$$

from bromide solution as $[Cr(NH_3)_6][BiBr_6]$, which is distilled with alkali, and the ammonia is determined acidimetrically in the distillate (Z. anal. Chem. 1933, **93**, 433).

(*c*) Bismuth is precipitated by oxine as $Bi(C_9H_6ON)_3$ and titrated [*see* Aluminium (*b*)] in solution exceeding $3N$- in acidity (Z. anal. Chem. 1927, **72**, 177; 1935, **103**, 261).

(*d*) $BiOCl$, precipitated in slightly acid tartaric acid solution, is collected, washed, dissolved in nitric acid, and the chloride determined by Volhard's method (Chem.-Ztg. 1933, **57**, 774).

Boron.—(*a*) *v.* Acidimetry and Alkalimetry (p. 645).

(*b*) Boric acid may be titrated in solution, carefully neutralised by iodate-iodide, by increasing the acid character of the boric acid by addition of mannitol.

To the borate solution, slightly acidified by hydrochloric acid, are added 5 c.c. of 10% barium chloride solution to remove carbon dioxide, followed by 20 c.c. of potassium iodide (2·5 g.) in saturated potassium iodate solution. Free iodine is then exactly removed by thiosulphate, and all boric acid is then liberated. A few drops of phenolphthalein are added, followed by $N/5$-sodium hydroxide from a burette until the solution is distinctly alkaline. A little mannitol is introduced, which bleaches the colour, and more alkali and mannitol are added in turn until the colour change is permanent: $B_2O_3=2NaOH$ (Amer. J. Sci. 1899, **7**, 147).

(*c*) Boron which has been separated as methyl borate (*see* Gravimetric Analysis, p. 591) is determined by diluting the methyl ester and methyl alcohol with water, allowing it to stand for a few minutes to complete its hydrolysis, adding mannitol and titrating as above.

Bromine.—A critical study (J. Appl. Chem. Russ. 1934, **7**, 852) of the methods of determining bromide in presence of chloride and iodide selects that of Szabo (Z. anal. Chem. 1931, **84**, 24) as the best. Iodide is removed as iodine by adding sodium nitrite and sulphuric acid and boiling. The bromide (<0·02 g.) is then oxidised to bromate by treatment with

2 g. of potassium bicarbonate and chlorine water, containing at least 0 3 g. of chlorine, and evaporation to dryness without boiling, and the bromate is determined iodimetrically.

Edwards, Nanji, and Parkes (Analyst, 1936, 61, 743) describe methods applicable to the determination of 10–100 mg. of bromide in presence of (i) 500 mg of chloride and/or (ii) 100 mg. of iodide (all as potassium salts). (i) The bromide in about 50 c.c. is oxidised by 2 c.c. of N potassium permanganate in presence of 1 c.c. of syrupy phosphoric acid, and the liberated bromine is at once rapidly aspirated during half an hour through two absorption tubes in series each containing 150 c c. of 1% potassium iodide solution, and the resulting iodine is titrated with 0 02N thiosulphate (ii) If iodide is present, it is oxidised to iodate by use of 9 c c. of the permanganate, and aspiration is started after 10 minutes' standing

Cadmium.—(i) To the solution, acidified with sulphuric acid and containing a few drops of sulphurous acid, 5 g of Rochelle salt and 3 g of potassium iodide, is added an aqueous 2 5% solution of phenyltrimethylammonium iodide After standing for at least 6 hours, the cream-coloured precipitate is filtered off on to a sintered glass crucible (Jena G4), and washed with 5 successive portions, each of about 5 c c, of a solution of 1 g of potassium iodide and 1 g. of the reagent in 200 c c. of water The precipitate is dried by suction as completely as possible, and then dissolved in the crucible in 20 c.c. of approximately 2N ammonia solution; the solution is sucked through and rinsed completely into a filter flask Hydrochloric acid is added in sufficient amount to be at least normal at the end of the titration, followed by 10% potassium cyanide (5 c.c.) and starch solution. The solution is then titrated with $M/40$ potassium iodate until the blue colour, which first develops, finally disappears. The reactions may be summarised thus.

$$[Ph(CH_3)_3N]_2CdI_4 \rightarrow 4NH_4I \rightarrow 4HI$$
$$2[2HI+HIO_3+3HCN=3ICN+3H_2O]$$

Zinc does not interfere. The method can be applied to the determination of cadmium in spelter and in zinc ores, interfering elements being removed by means of metallic iron (Analyst, 1933, 58, 667). β-Naphthaquinoline has been used similarly in the determination of cadmium in presence of zinc (Ber. 1927, 60, 1664); the 2 5% reagent solution (in $N/2$-sulphuric acid) is added to the cadmium solution prepared as above, together with a few drops of sulphurous acid solution. After 20 minutes the precipitate $(C_{13}H_9N)_2H_2CdI_4$ is collected, washed with 10 c c. of $N/5$ potassium iodide, 10 c.c. of the reagent solution, and 2 drops of dilute sulphurous acid diluted to 100 c.c., and is then decomposed and titrated as above.

(ii) Cadmium can be determined as described under Cobalt (*d*) (p. 656), but in this case the precipitate is $Cd(C_5H_5N)_2(CNS)_2$ (Z. anal. Chem. 1934, 99, 26).

(iii) Saturated ammonium carbonate precipitates cadmium carbonate, but not zinc or copper carbonate; the $CdCO_3$ can be washed, dissolved in standard acid, and the excess acid titrated (1934 A, 1191)

Calcium.—*By permanganate.*—The oxalate, precipitated from a hot slightly ammoniacal solution (*see* Gravimetric Methods, p 588), is washed with warm water till free from ammonium oxalate, decomposed with hot dilute sulphuric acid, and the oxalic acid titrated with $N/10$ permanganate. The precipitate may also be dissolved in dilute hydrochloric acid, and the solution titrated with permanganate, 0 5 g of manganese sulphate being added if this acid is used

Free Lime in cement and sand bricks is completely extracted by warming at 60°–80°C. for several hours with glycerol. The solution after dilution with alcohol is titrated with benzoic acid (J S C.I. 1930, 49, 360T). Another method, used for fertilisers, is described on p. 644).

Carbon.—CARBON DIOXIDE *v.* ACIDIMETRY AND ALKALIMETRY (p. 645), and GAS ANALYSIS (p 677).

CYANOGEN ACIDS. CYANATES —The cold, dilute solution is exactly neutralised with $N/10$-hydrochloric acid (using methyl orange or Congo red as indicator), excess of acid is added, the solution boiled for ten minutes, cooled, and titrated back by $N/10$ sodium hydroxide. Excess of $N/10$ sodium hydroxide is then added, the solution boiled to expel ammonia, and titrated back with $N/10$ hydrochloric acid. From these data two values for the cyanate can be calculated, which serve to check one another (Chem News, 1906, 93, 5, *cf* Z angew Chem. 1901, 24, 585, J. Soc Chem Ind 1904, 23, 244).

$$KCNO+2HCl+H_2O=KCl+NH_4Cl+CO_2$$

CYANIDES —(*a*) *By Precipitation* —(i) Excess of $N/10$ silver nitrate is added to the neutral cyanide solution, and then a little nitric acid The excess of silver is titrated with $N/10$ thiocyanate after filtering off the silver cyanide. (ii) The neutral solution (0 2–0 3 g. HCN in 250 c c) is treated with 5 c c each of 10% potassium iodide and 10% sodium hydroxide and titrated with $N/10$ silver nitrate with constant stirring till a permanent turbidity is produced, as shown best by using a black background. This marks the end of the reaction:

$$2KCN+AgNO_3=KNO_3+KAg(CN)_2$$

(*b*) *See* Ferrocyanides (*c*) (p 655).

(*c*) *Determination in Presence of Silver and Chlorides.*—The excess of cyanide above that required to form $KAg(CN)_2$ is titrated by $N/10$ iodine in presence of 5 g. of sodium chloride and a few drops of dilute ammonia until a faint permanent turbidity is produced; the reaction is $KCN+I_2=KI+ICN$.

The solution is then diluted to about 1 litre with tap-water, starch solution is added, and titration is continued with $N/10$ iodine until the solution turns blue:

$$KAg(CN)_2+2I_2=KI+AgI+2ICN$$

(J C S. 1929, 2037).

FERRICYANIDES —(*a*) The salt is reduced to ferrocyanide by boiling with sodium hydroxide; the filtered solution is strongly acidified with sulphuric acid and titrated with $N/10$ permanganate (*v.* Ferrocyanides (*a*)). Reduction may also be effected by boiling with sodium peroxide (Arch. Pharm. 1894, 232, 226).

(*b*) *Iodimetrically.*—The ferricyanide in 25 c.c. of $2N$-sulphuric or hydrochloric acid is mixed with 2–3 g. of potassium iodide and 2 g. of zinc sulphate, and the iodine liberated is titrated by $N/10$-thiosulphate in presence of starch (Z. anal. Chem. 1921, 60, 454).

FERROCYANIDES.—(*a*) *By Oxidation.*—The solution (150 c.c.) in approximately N-sulphuric acid is titrated with $N/10$-permanganate or ceric sulphate in presence of 5 drops of 1% diphenylamine solution until the colour changes from yellowish-green to a deep brown (Analyst, 1929, 54, 461).

(*b*) *Iodimetrically.*—Excess of $N/10$-iodine is added to the neutral solution (150 c.c.) at 40°C., and the excess is determined by thiosulphate in presence of starch, the colour of the solution finally becoming a clear yellowish-green.

(*c*) *By Conversion into Hydrocyanic Acid.*—The ferrocyanide solution is boiled for 5 minutes with 10 c.c. of N-sodium hydroxide and 15 c.c. of $3M$-magnesium chloride, 100 c.c. of boiling $M/10$-mercuric chloride are then added, and the boiling continued for 10 minutes. The mercuric cyanide produced is distilled for 30 minutes with 30 c.c. of $4N$-sulphuric acid, the hydrocyanic acid collected in 25 c.c. of N-sodium hydroxide, a little potassium iodide added, and the cyanide titrated with $N/10$-silver nitrate (Feld, Chem. Zentr. 1903, ii, 1398 ; Analyst 1908, 33, 261 ; 1910, 35, 295).

THIOCYANATES.—(*a*) *By Precipitation.*—As in standardising ammonium thiocyanate solution ; the thiocyanate must be added to the silver nitrate, and not *vice versâ*, since nitric acid decomposes thiocyanates.

(*b*) *By Oxidation.*—(i) The thiocyanate is titrated in concentrated hydrochloric acid solution with potassium iodate, in a stoppered bottle, with vigorous shaking. The end-point is reached when 5 c.c. of chloroform previously introduced are no longer coloured by iodine (J. Amer. Chem. Soc. 1908, 30, 760). The concentration of the acid should be 4–5N. The method is usually applied to cuprous thiocyanate :

$$4CuCNS+7KIO_3+14HCl$$
$$=4CuSO_4+7KCl+7ICl+4HCN+5H_2O;$$

but this is not typical, as the cuprous ion is also oxidised. (ii) The thiocyanate solution is treated with 1 c.c. of syrupy phosphoric acid and sufficient bromine to give a yellow colour. After 2 minutes 2 c.c. of saturated aqueous phenol solution are added and, after the mixture has stood for 15 minutes in the dark, potassium iodide is added and the liberated iodine titrated by thiosulphate :

$$KCNS+4Br_2+4H_2O$$
$$=KHSO_4+7HBr+BrCN$$
$$BrCN+2KI=KBr+KCN+I_2$$

Cyanide does not interfere (Z. anal. Chem. 1923, 62, 337).

Cerium.—(*a*) *Iodimetrically.*—Ceric oxide is warmed with concentrated hydrochloric acid and potassium iodide in a stoppered bottle until complete solution is effected. The liberated iodine is then titrated with $N/10$-thiosulphate. In order to oxidise cerous salts prior to use in this method, 200 c.c. of solution, containing about 0·2 g. of cerium, are treated first with 5 c.c. of concentrated sulphuric acid, then with 3 g. of ammonium persulphate, followed by a few drops of $N/10$-silver nitrate ; it is then boiled for 10 minutes, cooled, and titrated after addition of potassium iodide (Annalen, 1858, 105, 49 ; J. Amer. Chem. Soc. 1928, 50, 1379).

(*b*) *By Ferrous Sulphate.*—The cerium is oxidised by sodium bismuthate (J. Amer. Chem. Soc. 1909, 31, 523) in boiling sulphuric acid solution to ceric sulphate, and the filtered solution is reduced by adding standardised ferrous sulphate until the deep orange colour has nearly faded. Ten drops of 0·1% aqueous xylene cyanol FF are then added, and titration is continued until the orange colour changes sharply to green.

(*c*) *By Permanganate.*—Ceric salts are reduced by addition of an excess of standardised hydrogen peroxide ; when the yellow colour has disappeared, the excess is titrated by $N/20$ permanganate (not stronger) (Z. anal. Chem. 1897, 36, 685 ; 1903, 42, 448).

Chlorine.—*v. Halogens.*

Chromium.—The chromium should be in the form of chromate.

(*a*) *Iodimetrically.*—(i) To the chromate in approximately $N/2$-hydrochloric acid are added 2 g. of potassium iodide. After standing for a few minutes, the solution is diluted and the liberated iodine titrated by $N/10$-thiosulphate in presence of starch : $3I_2=2Cr$. For accurate results, it is best to displace air and maintain an atmosphere of carbon dioxide by addition of a few small portions of sodium bicarbonate to the acid solution.

(ii) Snethlage (Rec. trav. chim. 1934, 53, 567) finds sulphuric preferable to hydrochloric acid : the equivalent of 200 mg. of $K_2Cr_2O_7$ in 50 c.c. of water is treated with 4 c.c. of $9N$-sulphuric acid in a large long-necked flask, and 50 c.c. of $0{\cdot}4N$-potassium iodide are slowly (about 20 seconds) poured down the neck into the swirling liquid. The liberated iodine can be titrated forthwith.

(*b*) *By Reduction* (i) with ferrous ammonium sulphate, of which a slight excess is added to the chromate solution containing sulphuric or hydrochloric acid, the excess of ferrous salt being then titrated with $N/10$-dichromate ; (ii) with titanous chloride (*v.* PREPARATION OF STANDARD SOLUTIONS (p. 649) ; *also* J.S.C.I. 1908, 27, 673).

Chromium in Chrome Steel, Stainless Steels, and Ferrochrome.—(i) The sample (0·2 g.) is dissolved in a minimum of nitric acid (sp.gr. 1·2) ; if it is insoluble, procedure (ii) is used. The solution is diluted to 50 c.c., 1 g. of silver nitrate and 10 g. of ammonium persulphate are added, and the solution is boiled for 5 minutes. Ammonium chloride (0·25 g.) is added and the solution, containing precipitated silver chloride, is boiled to decompose any permanganic acid. After cooling and dilution to a definite volume, an aliquot portion is titrated as in (*b*) (i) above (J.C.S. 1907, 91, 1846).

(ii) To a 0·5-g. sample of the finely divided steel in a conical flask (500 c.c.) are added 10 c.c. of a mixture of 1 vol. of 72% perchloric acid and 2 vols. of 85% phosphoric acid. The mixture is heated at 175°–185°C. for 3–5 minutes ; the

steel dissolves completely and all chromium is in the tervalent condition. 15 c c. of a mixture of 1 vol. of 72% perchloric acid and 2 vols. of 80% sulphuric acid are added and the temperature is raised to 205°C.; oxidation to Cr^{VI} is complete after 10 minutes. Potassium permanganate (10–20 mg) is added, and the solution is rapidly cooled in ice cold water. It is then boiled for 5 minutes after dilution to 60–70 c.c. with water and addition of 0 5 c c. of concentrated hydrochloric acid. It is finally cooled by diluting to 250 c.c. with ice cold water and titrated as in (*b*) (i) above (J.S C I 1935, 54, 185; Ind. Eng. Chem. [Anal.], 1930, 2, 126; *see also* Analyst, 1934, 59, 609)

See also Manganese and Vanadium.

Chromium in Chrome Tanned Leather.—The leather is destroyed and the chromium is oxidised by perchloric acid in presence of osmic acid as catalyst; chromate is then titrated (J. Amer Leather Chem Assoc. 1935, 30, 442).

Chromium in Chromite.—The valuation of this, the only important ore of chromium, is usually effected by a volumetric method The finely powdered ore is fused with potassium pyrosulphate in a silica crucible. The melt is leached *with dilute sulphuric acid, metals precipitated* by hydrogen sulphide are removed, and after oxidation with nitric acid, chromium and other hydroxides are precipitated by ammonia The precipitate is filtered off, washed, dissolved in dilute perchloric acid, evaporated until oxidation to chromate is effected, and then titrated as above.

Cobalt.—(*a*) The cobalt solution in a 500 c c. conical flask, containing 1–2 g of sodium perborate, is neutralised with 6*N*-sodium hydroxide and a further 10 c c. are added, $Co(OH)_3$ is precipitated with effervescence. The mixture is boiled for 10 minutes to decompose excess perborate and, whilst the solution is still boiling, the flask is closed by a rubber stopper carrying a tap funnel with its tap open As soon as heating is stopped, the tap is closed and a measured volume of standard ferrous sulphate in excess is placed in the funnel. The tap is opened and the solution is drawn into the flask, but air is not allowed to enter. The funnel is rinsed with water, similarly added, the flask is shaken, and 25 c.c. of 6*N*-sulphuric acid are run in, the precipitate rapidly dissolving After the flask has cooled to room temperature, the stopper is removed, 3–4 c.c. of syrupy phosphoric acid are added, and the excess ferrous iron is titrated with *N*/10 dichromate *with barium diphenylaminesulphonate as indicator*: Co=Fe (Sarver, Ind. Eng. Chem. [Anal.], 1933, 5, 275; *see also* J. Amer. Chem. Soc. 1922, 44, 2237; Ind. Eng. Chem 1916, 8, 901; Natuurwetensch. Tijds. 1929, 11, 123).

(*b*) *By Double Cyanide Formation.*—*See* Nickel (*a*) (p 663), but the cobalt complex requires **5KCN** per atom of cobalt.

(*c*) *By Precipitation* with ferrocyanide, as described under Nickel (*b*).

(*d*) In presence of pyridine, a measured excess of standard thiocyanate precipitates

$$Co(C_5H_5N)_4(CNS)_2,$$

which is filtered off, the excess thiocyanate being determined by silver nitrate (Ind. Eng Chem [Anal.], 1934, 6, 459; *see also* Spacu and Kuraš, Bull. Soc. Ştiinţe Cluj, 1934, 7, 377)

Cobalt in Ores—*See* J. Iron and Steel Inst. 1918, 97, 441; Analyst, 1919, 44, 276.

Copper.—(*a*) *Iodimetrically.*—To the solution (25 c c) of cupric salt, preferably neutral or containing acetic acid, are added 2–3 g. of potassium iodide, and the liberated iodine is titrated by *N*/10-thiosulphate, starch being added towards the end of the reaction:

$$2CuSO_4+4KI=2K_2SO_4+2CuI+I_2$$

The end-point is improved by addition of 1 drop of *N*/10 silver nitrate or a few c c of *N*/10-potassium thiocyanate added near the end point (J. Amer. Chem. Soc 1935, 57, 845; Chem. Weekblad, 1935, 32, 509).

(*b*) *By Titration with Potassium Cyanide (Steinbeck's Process)*—The ammoniacal copper solution is titrated with potassium cyanide until colourless (*v* Brearley, Chem News, 1897, 76, 189; it should contain 2 5% of ammonium chloride to avoid low results (Chem.-Ztg 1934, 58, 712)

(*c*) *By Precipitation as Thiocyanate*—The pre*cipitated* **CuCNS** *(see p. 586) is filtered off on* asbestos, the mat transferred to a bottle and titrated THIOCYANATES (p 655)

(*d*) *By Reduction to Cuprous Salts*—To the sulphuric or hydrochloric acid solution, 10–20 c c. of 10% potassium thiocyanate and a little ferrous salt are added, a deep red coloration is produced, since ferrous salts in acid solution are partly oxidised by cupric salts The cold solution is titrated with titanous chloride until the red coloration is destroyed (J C S 1906, 89, 1491) Alternatively, a slight excess of titanous chloride may be added, and titrated back with standard ferric alum.

Fluorine.—(*a*) *By Precipitation as Lead Chlorofluoride.*—To the neutral solution (250 c c.), containing 0 01–0 1 g. of fluoride ion, are added 10% sodium chloride (3 c.c) and nitric acid until the solution is just acid to bromophenol blue, followed by sodium hydroxide until it is just alkaline. Concentrated hydrochloric acid (1 c c.) and lead nitrate (5 g) are added, the solution is heated, and as soon as the solid has dissolved, sodium acetate (5 g) is stirred in. Heating is continued on a steam bath for 30 minutes and the solution is allowed to stand overnight. The supernatant liquid is decanted through a filter (Whatman No 42) and the **PbClF** is washed once with cold water, then *four times with a cold saturated solution of* lead chlorofluoride, and finally with cold water. The filter paper and precipitate are placed in the beaker in which precipitation was carried out, 100 c c. of nitric acid (5%) are added, and the mixture is heated on a steam-bath with stirring for 5 minutes to disintegrate the paper and to dissolve the precipitate. Silver nitrate solution (*N*/10) is added in slight excess and heating is continued for 30 minutes. The solution is then cooled, silver chloride is filtered off, and the excess silver is titrated by *N*/10 thiocyanate, 1 c.c. of *N*/10 silver nitrate=0 0019 g. of F'. Aluminium and iron must be absent, but phosphates, carbonates, sulphates, and chromates are

without effect (Bur. Stand. J. Res. 1929, **3**, 581 ; Z. anal. Chem. 1933, **95**, 225 ; 1934, **99**, 21 ; Z. anorg. Chem. 1911, **70**, 173 ; J. Amer. Chem. Soc. 1915, **37**, 2509 ; Ind. Eng. Chem. 1924, **16**, 938 ; 1926, **18**, 573).

(*b*) *Iodimetrically.*—Ferric fluoride, unlike ferric chloride, does not liberate iodine from potassium iodide.

The fluoride solution (100 c.c.) in a stoppered bottle is made just acid to methyl red by hydrochloric acid, and there are added 20 c.c. of 20% sodium chloride solution and a measured excess of 0·08*M*-ferric chloride solution, followed by 2 c.c. of *N*-hydrochloric acid and 10 c.c. of 5% potassium iodide solution. The bottle is immersed in water at 38°C. for 30 minutes, then cooled rapidly and the iodine titrated by *N*/30-thiosulphate. A blank is carried out on the ferric chloride under identical conditions and fluoride is obtained by difference : $Fe=3F$ (Ind. Eng. Chem. 1931, **23**, 996 ; Ber. 1913, **46**, 2511).

(*c*) A volumetric process, almost specific for fluorides, depends on the use of standard thorium nitrate, with zirconium alizarin-sulphonate as indicator. The latter reagent is made by mixing 3 parts of a solution of 1 g. of $Zr(NO_3)_4,5H_2O$ in 250 c.c. of water with 2 parts of a solution prepared from 1 g. of sodium alizarinsulphonate treated with 100 c.c. of ethyl alcohol, filtered, and 150 c.c. of ethyl alcohol added ; the resulting solution is coloured violet-red. To a soluble fluoride solution (about 20 c.c.) are added 3 drops of indicator and just sufficient dilute hydrochloric acid to destroy the colour. After introduction of an equal volume of ethyl alcohol, the solution is titrated with standard thorium nitrate (*N*/10 or *N*/100, standardised by pure sodium fluoride as in the method) until the colour reappears.

When interfering elements are present, the fluoride is first distilled with perchloric acid and glass, sufficient water being added to make the solution boil at 110°C., and distillation is continued until the temperature reaches 135°C. More refractory fluorides are first broken up by alkali fusion (Ind. Eng. Chem. [Anal.], 1933, **5**, 7, 17 ; Z. anorg. Chem. 1926, **152**, 213).

(*d*) A rapid method (J. Appl. Chem. Russ. 1933, **6**, 939) consists in adding to the fluoride solution an excess of silica, followed by concentrated hydrochloric acid in slight excess as denoted by methyl orange ; after being made neutral by 0·5*N*-potassium hydroxide, the solution is treated with 10 c.c. of 4*N*-calcium chloride and titrated (to phenolphthalein) with alkali : $OH'=F'$.

Gallium.—*By Oxine.*—*See* Z. anorg. Chem. 1932, **209**, 129.

Gold.—(*a*) *Iodimetrically.*—The auric solution, containing about 0·015 g. of gold in 25 c.c. of solution, is treated with potassium iodide in more than sufficient quantity to dissolve the aurous iodide first precipitated, and the iodine liberated is estimated with *N*/100-thiosulphate (Amer. J. Sci. 1899, **8**, 261 ; Z. anorg. Chem. 1899, **19**, 63).

(*b*) *By Permanganate.*—The auric chloride solution (free from nitrate and nearly neutralised to ammonia) is treated with *N*/10-potassium oxalate or *N*/10-ferrous sulphate (in feebly acid solution) and kept on the steam-bath until all the gold is precipitated ; the excess of precipitant is then titrated by *N*/10-permanganate.

Halogens.—The term is restricted in this connection to chlorine, bromine, and iodine, fluorine being treated separately, since its analytical reactions are quite different.

Estimation of Halogens.—*Iodine* is estimated by solution in potassium iodide and titration with *N*/10-thiosulphate (*v.* Preparation of Standard Solutions (p. 648)). *Bromine* and *chlorine* are absorbed in potassium iodide solution setting free an equivalent quantity of iodine, which is titrated with thiosulphate.

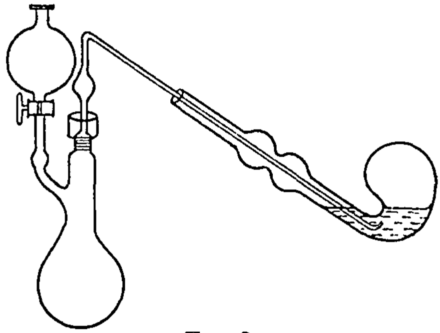


Fig. 3.

A large number of substances, *e.g.* peroxides, chlorates, chromates, etc., may be readily determined indirectly by distillation with concentrated hydrochloric acid, the available oxygen of the compound setting free its equivalent of chlorine, which is absorbed in potassium iodide, and the liberated iodine titrated with *N*/10-thiosulphate. It is necessary to exclude air in the process of distillation, since it liberates iodine from hydrogen iodide set free in the receiver, by the hydrogen chloride distilling over during the experiment. The apparatus originally designed by Bunsen for this purpose is now rarely used. The absorption vessel is retained in Hempel's modification of it (Fig. 3), but it is often preferable to use two sets of absorption bulbs in series (Fig. 4), and Bunsen's small flask, connected to a delivery tube by a wide piece of rubber tubing, is now always replaced by a flask with a ground-in delivery tube, sometimes with a cup for a water seal. The flasks are designed for controlled addition

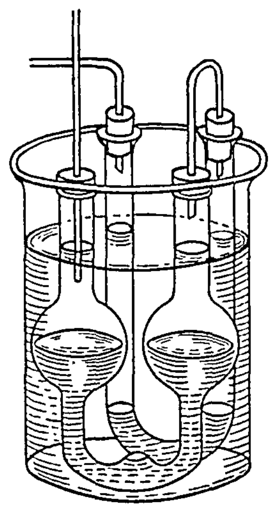


Fig. 4.

of acid (Fig. 4), and a particularly useful form, shown in Fig. 5 (Analyst, 1908, 33, 117), admits of the passage of a current of steam, carbon dioxide, or other gas during the distillation.

ESTIMATION OF HALOGENS IN HALIDE SALTS. —*By Precipitation*.—(i) *Mohr's Method*.—The neutral solution is titrated with $N/10$ silver nitrate in the presence of a few drops of potassium chromate as indicator (v. PREPARATION OF STANDARD SOLUTIONS (p. 649). It is advisable to perform a blank experiment under identical conditions, to allow for the silver nitrate necessary to bring out the reddish coloration. The end point is poor for iodide solutions.

(ii) *Adsorption Indicators* (v. PREPARATION OF STANDARD SOLUTIONS (p. 650)).—*Chloride, bromide, and iodide* may be titrated by standard

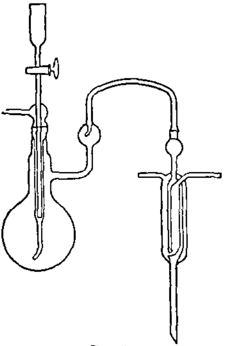


FIG. 5.

silver solutions with fluorescein or dichlorofluorescein as indicator. With a suitable choice of indicator, one halide may be titrated selectively in presence of another, *e.g.* iodide may be titrated in presence of chloride with Rose Bengal as indicator (*see* p. 659). Chloride and bromide may be titrated with standard mercurous nitrate with bromophenol-blue as adsorption indicator (Z. anorg. Chem. 1929, 184, 237; J. Amer. Chem. Soc. 1934, 56, 1881). Other halide or thiocyanate titrations involve, for example, the use of tartrazine and phenosafranine (Analyst, 1930, 55, 613), Victoria-violet (Chem. Weekblad, 1929, 26, 6), and diphenylcarbazide or diphenylcarbazone (Z. angew. Chem. 1929, 42, 284, 429; Mikrochem. 1932, 12, 315; 1934, 15, 95; Analyst, 1933, 58, 331; Z. anal. Chem. 1933, 93, 345; 1935, 101, 31).

(iii) *Volhard's Method*.—The nitric acid solution of the halide is precipitated by adding a slight excess of $N/10$ silver nitrate, the excess being then titrated with $N/10$ ammonium thiocyanate. Silver chloride must be filtered off, or coagulated by boiling or shaking with a few c.c. of ether or nitrobenzene, before the titration is performed; but silver bromide and iodide do not undergo a corresponding complicating reaction with thiocyanate. It is advisable to titrate iodide in a stoppered bottle with vigorous shaking when adding both the silver solution and the thiocyanate, to minimise error due to occlusion. It is more accurate to weigh out a very slight excess of pure silver, dissolve it in nitric acid (carefully expelling nitrous acid, which interferes with the indicator), and add to the halide solution than to measure out $N/10$ silver nitrate. After vigorous shaking, the excess of silver is then titrated with a dilute thiocyanate solution (1 c.c.=1 mg Ag).

IODIDES.—*Iodimetrically*.—(i) A slight excess of potassium iodate is added, and the solution acidified with dilute sulphuric acid. The liberated iodine is extracted with chloroform, carbon disulphide or toluene, the extract is separated, and titrated with $N/10$ thiosulphate. A weaker acid than sulphuric may be employed, *e.g.* acetic or tartaric acid. Five-sixths of the iodine found was originally present as iodide. This method is available in the presence of bromide and chloride, if acetic acid be employed.

(ii) *Andrews' Method*.—To the iodide solution, occupying about 100 c.c. in a stoppered bottle, are added an equal volume of concentrated hydrochloric acid and 5 c.c. of carbon tetrachloride or chloroform. Standard potassium iodate ($M/40$ or $M/20$) is run in with swirling until the solution, which is at first strongly coloured with iodine, becomes pale brown. Additions of iodate are continued until the violet colour of the solvent layer is only faint, and then drop by drop, shaking after each drop, until the solvent layer loses the last trace of violet. The reaction may be summarised thus:

$$2HI+HIO_3+3HCl=3ICl+3H_2O$$

Ceric sulphate or chloramine T may be used instead of potassium iodate. Lang's estimation, based on the analogous reaction

$$2HI+HIO_3+3HCN=3ICN+3H_2O,$$

is carried out as follows: To the iodide solution, contained in a long-necked flask, is added sufficient hydrochloric acid to make the acidity approximately normal at the end of the titration. 5 c.c. of 10% potassium cyanide and starch solution are introduced, and the solution is titrated by standard potassium iodate until the blue colour disappears (J. Amer. Chem. Soc. 1903, 25, 756; Z. anorg. Chem. 1922, 122, 332; J. Amer. Chem. Soc. 1930, 52, 899; Analyst, 1934, 59, 736).

ESTIMATIONS OF HALOGENS IN OXYHALOGEN COMPOUNDS.—(a) *By Reduction* to a halide salt and determination of the latter. *Iodates* are reduced by adding sulphurous acid to the sulphuric acid solution of the iodate until the separated iodine is redissolved; an excess of $N/10$ silver nitrate is added to precipitate the iodide, the mixture boiled with excess of nitric acid, and finally the excess of silver titrated with $N/10$ thiocyanate. *Bromates and chlorates* are reduced by adding an excess of iron filings

to the sulphuric acid solution; after an hour, excess of $N/10$-silver nitrate is added, the mixture boiled with nitric acid to oxidise the ferrous salt, and the excess of silver titrated (Amer. Chem. J. 1904, **32**, 242). *Chlorates* in 25% sulphuric acid solution are reduced to chloride by 10 minutes' shaking with zinc amalgam; *bromates* and *iodates* are reduced in 3 minutes in $3{\cdot}5N$-acid solution. Jannasch (Ber. 1905, **38**, 1576) uses hydroxylamine sulphate and excess nitric acid for *chlorates*, or hydroxylamine in ammoniacal solution for *bromates* and *iodates*. Formaldehyde in dilute nitric acid reduces *chlorates* in ½ hour, *bromates* in 2½ hours, but not *iodates*.

(*b*) *By Reduction* to a halide salt and estimation of the reducing agent used up in the process. With *chlorates* and *bromates*, the sulphuric acid solution is boiled for 10 minutes with excess of standard ferrous sulphate in an atmosphere of carbon dioxide, the solution cooled, and the unchanged ferrous salt titrated with $N/10$-$K_2Cr_2O_7$: $6Fe{=}ClO_3$ or BrO_3. *Bromates* may also be reduced with arsenious oxide (Amer. J. Sci. 1902, **14**, 285). *Chlorates* are reduced by the same reagent in presence of osmic acid as catalyst (Z. anal. Chem. 1933, **95**, 385), and also by adding an excess of $N/10$-titanous sulphate, and after 3 minutes titrating back with ferric alum (J.S.C.I. 1908, **27**, 434).

(*c*) *Iodimetrically. Chlorates.*—(i) By distillation with concentrated hydrochloric acid: $ClO_3{=}3I_2$ (*Bunsen's Method*; *v.* ESTIMATION OF HALOGENS, (p. 657); J.C.S. 1892, **61**, 87). (ii) To the chlorate solution in a stoppered bottle are added twice its volume of concentrated hydrochloric acid and 1 g. of potassium bromide. After 5 minutes, potassium iodide (1 g.) is added and the liberated iodine is titrated, after dilution, by standard thiosulphate: $ClO_3{=}3I_2$ (Chem.-Ztg. 1901, **25**, 727).

Hypochlorites.—(i) A slight excess of $N/10$-sodium arsenite is added and the excess titrated with $N/10$-iodine, or the hypochlorite is directly titrated with the arsenite till a drop of the solution ceases to colour starch–potassium iodide paper blue: $As{=}ClO'$ (*Penot's Method*; *cf.* Chem.-Ztg. 1904, **28**, 59). (ii) An excess of potassium iodide solution is added, followed by acidification with acetic acid. The liberated iodine is titrated by standard thiosulphate.

Perchlorates.—The concentrated solution is boiled with a large excess of titanous sulphate, the excess oxidised with permanganate, and the chloride produced is titrated as usual (Z. anorg. Chem. 1909, **62**, 108; Chem.-Ztg. 1909, **33**, 759).

Bromates.—The substance is treated as in (*c*) (ii) above in presence of a few drops of ammonium molybdate solution. Reaction is very rapid (Z. anal. Chem. 1921, **61**, 348).

Iodates.—These are simply added to a slight excess of potassium iodide solution, acidified with sulphuric or hydrochloric acid, and the liberated iodine titrated: $IO_3{=}3I_2$.

Periodates.—Determination is based on the reaction:

$$HIO_4+7HI=4I_2+4H_2O$$

The acidified mixture of periodate and potassium iodide is warmed at 60°C. in a stoppered bottle for 15 minutes, cooled, and the iodine titrated (J.C.S. 1934, 1087).

ESTIMATIONS INVOLVING MIXTURES OF THE FOREGOING HALIDES SALTS.

Chloride, Hypochlorite, and Chlorate.—The solution is titrated with $N/10$-sodium arsenite by Penot's method for the *hypochlorite*; the *chlorate* is then estimated in the solution, after acidifying with sulphuric acid, by reduction with standard ferrous sulphate; the *total chloride* then present is titrated by Volhard's method.

Chloride, Chlorate, and Perchlorate.—*Chloride* is titrated in one portion of the solution by Volhard's method, and in another portion after reducing the *chlorate* with ferrous sulphate. For *perchlorate* the dry substance is mixed with five times its weight of pure quartz sand in a platinum crucible and covered with a layer of the sand 2 cm. deep; the bottom of the crucible is heated to redness for half an hour, the mixture is cooled, extracted with water, and the total chloride estimated (Compt. rend. 1896, **122**, 452).

Chloride and Iodide.—The *total halogen* is titrated by a suitable method in one portion of solution, and the *iodide* in another portion is determined either by (*a*) procedures described for Iodide (ii) (p. 658) or (*b*) titration of the iodide selectively in the mixture; 25 c.c. of the neutral solution of chloride and iodide, containing 3 drops of 0·5% aqueous Rose Bengal, are titrated by $N/10$-silver nitrate until the colour change carmine to violet-blue takes place (Z. anorg. Chem. 1924, **137**, 233; Analyst, 1936, **61**, 315).

Bromide and Iodide may be determined as under Chloride and Iodide (*a*) above.

Bromide and Chloride.—The methods are analogous to those described below for Chloride, Bromide, and Iodide. (i) The solution is placed in a flask fitted with a ground-in stopper, dropping funnel, and delivery tube. One-third of its volume of concentrated sulphuric acid is added, with cooling, followed by 5 g. of chromic acid. The delivery tube is jointed to a vessel containing a measured volume of standard sodium arsenite solution, a few grams of sodium bicarbonate, and water to a total volume of about 200 c.c. Air is aspirated through the solution for 1 hour, and the excess arsenite is then titrated by standard iodine.

If only small amounts of bromide relative to chloride are present, the bromine evolved, together with some chlorine, is absorbed in 40 c.c. of 0·5% sodium hydroxide. Saturated sulphurous acid (1–2 drops) is then added and the solution is neutralised with $10N$-sulphuric acid and placed in a clean reaction flask. Liberation of bromine and absorption in arsenite are then carried out as above. Total chloride and bromide are determined in another portion of solution (Analyst, 1931, **56**, 590; Z. anorg. Chem. 1895, **10**, 387; Z. anal. Chem. 1921, **60**, 405; Gazzetta, 1883, **13**, 174; Ind. Eng. Chem. 1919, **11**, 954).

Chloride, Bromide and Iodide.—The iodide is first selectively oxidised by arsenic acid to iodine,

which is removed in a current of air and estimated. Bromine is then similarly estimated after liberation by chromic acid, and chloride is determined as silver chloride, precipitated from the residual solutions.

The halide solution, diluted to 100 c.c., is contained in a flask fitted with a dropping funnel and delivery tube connected to an absorption tube containing 10% potassium iodide, and a guard-tube, filled with glass beads moistened with the same solution. Potassium arsenate (2 g.) and 18N-sulphuric acid (25 c.c.) are added through the funnel. The solution is warmed, the liberated iodine is aspirated into the iodide solution, and titrated by standard thiosulphate. The volume of liquid in the flask is maintained during the experiment by addition of water, and must not be allowed to fall below half its initial bulk, otherwise bromine is then liberated.

A solution containing 10 g. of potassium dichromate is added to the residual solution, which is then diluted with water to 200 c.c. Bromine is then distilled, collected and titrated as described in the preceding section (Z. anorg. Chem. 1892, 1, 419). Many of the methods described in the gravimetric section for determining chloride, bromide and iodide in admixture are readily adapted to volumetric treatment.

Indium.—Indium, as acetate, is titrated by potassium ferrocyanide, containing a small amount of potassium ferricyanide, with diphenylbenzidine as internal indicator. Interfering elements are first separated by hydrogen sulphide, from 1N-acid solution, followed by precipitation of indium as hydroxide; iron, if present, is rendered inactive by addition of sodium fluoride; chlorides must be absent. The method can be used for the determination of indium in dental alloys (Ind. Eng. Chem. [Anal.], 1936, 8, 51).

Iron.—FERROUS SALTS.—*By Oxidation.*—(i) The cold solution is strongly acidified with dilute sulphuric acid and titrated with 0·1N-permanganate. This simple and accurate method requires modification when hydrochloric acid is present, since this reacts with permanganate, *especially in presence of iron salts. This side* reaction can be largely prevented by addition of manganese sulphate and phosphoric acid to the solution and titrating *very slowly*. The required solution, of which 25 c.c. suffice for a titration, contains 67 g. of crystallised manganese sulphate, 138 c.c. of phosphoric acid (sp.gr. 1·7), and 130 c.c. of concentrated sulphuric acid per litre. Scott (J. Amer. Chem. Soc. 1924, 46, 1396) improves the results by using a few drops of a 1% solution of diphenylamine in sulphuric acid as indicator. A 1% solution of brucine in sulphuric acid has been recommended for the same purpose, the acidity of the solution being kept above 3N with regard to sulphuric acid (Proc. Indian Acad. Sci. 1936, 3, A, 38; *see also* p. 647).

(ii) The acid solution is titrated by 0·1N dichromate as described on p. 647, this titration being available in presence of hydrochloric acid.

(iii) By ceric sulphate; *see* p. 648.

FERRIC SALTS.—(*a*) *By reduction* to ferrous salt and titration with permanganate or dichromate. Reduction may be effected in any of the following ways: (i) Hydrogen sulphide is passed through the cold sulphuric acid solution (N/2; 100 c.c.) for 30 minutes, and then for 15 minutes whilst the solution is boiled; 15 c.c. of sulphuric acid (1 : 1) are added, and the solution is boiled down in a current of carbon dioxide to about half bulk. Sulphur is coagulated and need not be removed before titration. (ii) The nearly neutral solution is boiled with sulphurous acid or ammonium sulphite, excess being removed by continued boiling, preferably in a current of carbon dioxide. (iii) 8–10 g. of granulated zinc are added to the warm sulphuric acid solution, and the action allowed to continue until a drop of the solution no longer gives a coloration with potassium thiocyanate. The solution is cooled, filtered through glass wool, and titrated. The use of zinc-copper

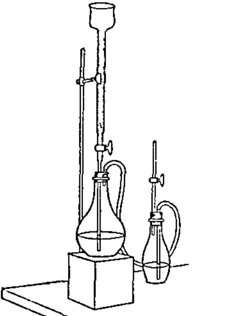


FIG. 6.

couple is preferable and magnesium powder brings about reduction rapidly and completely. Reduction may be rapidly effected by pouring the liquid through a column of amalgamated zinc about a foot long (The Jones Reductor, Fig. 6); Chem. News, 1889, 60, 93; Blair's "Chemical Analysis of Iron," 8th ed.). The apparatus is prepared for use by drawing 100–150 c.c. of c. 5% sulphuric acid through the column by application of water-pump suction, followed by two portions each of 50 c.c. of distilled water. Liquid is never allowed to drain below the bottom of the cup at the top of the reductor. In carrying out a reduction, liquids are drawn through at the rate of about 100 c.c. per minute in the following order: (1) 25–50 c.c. of 5% sulphuric acid; (2) the solution to be reduced, occupying about 100 c.c., and about normal with respect to sulphuric acid; (3) 100 c.c. of approximately N/2 sulphuric acid; (4) 100–150 c.c. of water. Hydrochloric acid may replace sulphuric acid. (iv) The

hydrochloric acid solution is heated nearly to boiling, and stannous chloride (25% solution) added drop by drop until the solution is colourless; 10 c.c. of saturated mercuric chloride are added to the cooled solution to destroy excess of stannous chloride, the solution diluted, and the ferrous salt titrated with $N/10$-potassium dichromate (*see* p. 647) with barium diphenylamine-sulphonate as indicator. (v) *Reduction by palladium-hydrogen* in boiling acid solution; this introduces no foreign substance into the solution (Z. angew. Chem. 1902, **15**, 398, 424; Analyst, 1904, **29**, 346).

(*b*) *By Direct Titration with a Reducing Agent.*—(i) *Titanous chloride.* The sulphuric or hydrochloric acid solution of the ferric salt is titrated as described under PREPARATION OF STANDARD SOLUTIONS (p. 649). (ii) *Stannous chloride.* The nearly boiling hydrochloric solution is titrated as described under PREPARATION OF STANDARD SOLUTIONS (p. 649).

FERROUS IRON IN MINERALS AND ROCKS.—The only satisfactory method consists in decomposing the coarsely powdered substance with sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide, and titrating the ferrous salt produced. (For an exhaustive discussion of this problem, *v.* Hillebrand and Lundell, "Applied Inorganic Analysis.")

Iron and Aluminium.—After weighing the ignited sesquioxides, they are brought into solution by fusion with potassium hydrogen sulphate. If iron and aluminium are in solution, iron can be determined volumetrically in an aliquot portion, and total iron and aluminium gravimetrically in a second portion.

Iron and Titanium.—*Ferric* salts can be reduced with sulphurous acid or hydrogen sulphide without reducing *titanic* salts; or reduction of both may be effected by means of the Jones Reductor, the *titanous* salt oxidised with a slight excess of bismuth oxide, and the *ferrous* salt titrated in the filtered solution. To estimate both elements present, one of the preceding methods may be combined with the reduction process for titanium, described later, which would give the *total iron and titanium* (*v. also* J.S.C.I. 1909, **28**, 189; Analyst, 1910, **35**, 198).

Iron and Vanadium.—(i) Reduction with sulphur dioxide proceeds with the vanadium as far as to the oxide V_2O_4; reduction with zinc carries it as far as V_2O_2; hence two such reductions and titrations with permanganate furnish data for calculating both iron and vanadium (Amer. J. Sci. 1908, **26**, 79). (ii) By reduction in a silver reductor, iron is converted into the bivalent and vanadium into the quadrivalent condition. Sulphuric acid is added to the reduced solution to give a concentration of $5N$, and iron is titrated by $N/10$-ceric sulphate with phenanthrolino-ferrous sulphate as indicator; vanadium is not oxidised. Titanium, manganese, and chromium are without effect, but molybdenum reacts (J. Amer. Chem. Soc. 1934, **56**, 350).

Lead.—*By Precipitation.*—(i) *As Molybdate.*—The boiling acetic acid solution (200 c.c.) is titrated with standard ammonium molybdate (9 g. per litre, titrated against a solution of pure lead). The solution is well shaken, allowed to stand for a few minutes, and a drop of the supernatant liquid is added to a drop of a solution of tannin (0·3%, containing a trace of lead); the end-point is shown by the appearance of a yellow colour, indicating that molybdate is present in excess. A mixture of stannous chloride and potassium thiocyanate dissolved in a little water can also be used as an external indicator, a red colour being obtained at the end-point. The indicators not being very sensitive, a "blank" experiment should be made and the necessary correction allowed for, both in an assay and in standardising the solution.

(ii) *As Ferrocyanide.*—The cold acetic acid solution is titrated with potassium ferrocyanide (10 g. per litre titrated against pure lead) until a drop of the solution produces a brown coloration with a drop of saturated uranium acetate solution; a "blank" experiment should also be made (J. Amer. Chem. Soc. 1893, **15**, 550; Chem. News, 1896, **73**, 18; J.C.S. 1893, **64**, 599; Ind. Eng. Chem. [Anal.], 1930, **2**, 124).

(iii) For various titration methods for lead in which adsorption indicators are used, *see* Z. anal. Chem. 1927, **164**, 219; 1934, **99**, 18; Trans. Faraday Soc. 1932, **28**, 561, 565; Analyst, 1933, **58**, 332; 1935, **60**, 316; Ann. Chim. Analyt. 1936, **18**, 33.

(iv) Lead is precipitated as $PbClF$ by addition of a measured excess of $0{\cdot}2N$-sodium chloride and $0{\cdot}2N$-sodium fluoride, the excess of chloride being determined in the filtered solution by means of silver; copper and zinc do not interfere (Z. anal. Chem. 1934, **99**, 18). In determining lead in ores, etc., it is usually separated as sulphate and dissolved in ammonium acetate previous to titration. In addition to the foregoing procedures, lead may be precipitated as oxalate from the solution so obtained, and the washed precipitate suspended in dilute sulphuric acid and titrated by permanganate.

Magnesium.—(*a*) *Iodimetrically.*—The magnesium is precipitated as magnesium ammonium arsenate, dissolved in hydrochloric acid and potassium iodide, and the iodine titrated (J. Amer. Chem. Soc. 1899, **21**, 746; Z. anal. Chem. 1907, **46**, 714; Angew. Chem. 1935, **48**, 551).

(*b*) *By Precipitation with Oxine.*—Magnesium is precipitated as $Mg(C_9H_6ON)_2$ from alkaline solution, the precipitate is dissolved in dilute hydrochloric acid solution, and the oxine determined bromometrically (*see* p. 650). Magnesium may be determined in presence of calcium, *e.g.* in cement, as follows:

To the boiling solution, after removal of alumina, etc., are added 1 c.c. of ammonia (sp.gr. 0·9) and 25 c.c. of hot 4% ammonium oxalate. After boiling for 2–3 minutes, the mixture is heated on the steam-bath for 10 minutes and then cooled to 70°C.; 20 c.c. of oxine solution (1·25% in $N/2$-acetic acid) are stirred in without removal of the calcium oxalate, followed by 4 c.c. of ammonia for each 100 c.c. of solution; stirring is continued for 15 minutes. The precipitate is filtered off, washed with dilute ammonia (1 : 40), dissolved and titrated with standard bromate and thiosulphate (Bur. Stand.

J. Res. *1931*, **6**, *113* ; *1933*, **10**, *823*). For bibliography, *see* Berg, "Das o Oxychinolin," Enke, 1935 ; "Organic Reagents for Metals," Hopkin and Williams, Ltd., 1934.

Manganese.—(*a*) *By Oxidation with Permanganate* (*Volhard's Method, Modified*).—To the feebly acid solution are added 2 g. of sodium acetate for each 10 c.c. of permanganate expected to be required and 5 g. of potassium fluoride (to render iron inactive and to aid flocculation). The solution is diluted to 300–400 c.c., heated and titrated slowly, with shaking, with $N/10$ permanganate until the supernatant liquid is just pink. A "blank" should be carried out on the reagents. The reaction

$$3MnO+Mn_2O_7=5MnO_2$$

proceeds quantitatively (Z. anal. Chem. 1926, **68**, 129 , 1909, **48**, 751 ; Analyst, 1911, **36**, 52 ; Bull Soc. chim. 1935, [v], **2**, 740).

(*b*) *By Precipitation as Dioxide* and estimation of the available oxygen. Precipitation may be effected by adding bleaching powder solution and calcium carbonate to a hot neutral solution of the manganese salt containing ferric and zinc chlorides J C.S. 1879, **35**, 365 ; J.S.C.I. 1891, **10**, 333), or by boiling a solution in concentrated nitric acid (free from hydrochloric acid) with potassium chlorate. The second method gives slightly low results, and a parallel determination should be carried out on a known amount of manganese The washed precipitate in either case is dissolved in a *sulphuric acid solution of standard ferrous sul* phate or oxalic acid, and the excess of reagent titrated.

(*c*) *By Conversion into Permanganic Acid.*—(i) The sulphuric acid solution is boiled with 10 c.c each of 25% ammonium persulphate solution and 0 8% silver nitrate solution, cooled, diluted, and titrated by sodium arsenite solution to a clear yellow end-point. Similar oxidation in phosphoric acid solution containing sodium pyrophosphate, followed by iodimetric determination of the permanganate is also recommended (Chem. Weekblad, 1934, **31**, 633). (ii) The cold solution free from hydrochloric acid, cobalt, and chromium, and containing one-quarter its volume of nitric acid (sp gr. 1·42), is oxidised by shaking with 2–4 g of sodium *bismuthate (equal to twenty-six times the weight* of manganese expected to be present) for 3 minutes, diluted with half its volume of 3% nitric acid, the solid residue allowed to settle, and the permanganic acid solution filtered into a slight excess of ferrous sulphate ; excess of the latter is then titrated with $N/10$ permanganate. A blank is carried out on the reagents exactly as in this procedure, and manganese is calculated from the difference between the titres (Dingl. polyt. J. 1888, **269**, 224 ; J.C.S. 1895, **67**, 268 ; Chem. News, 1901, **84**, 209, 247 ; J. Amer. Chem. Soc. 1904, **26**, 793 ; Ind. Eng. Chem. 1926, **18**, 597). (iii) Oxidation of manganese salts to permanganate is also effected by potassium periodate in presence of sulphuric or phosphoric acid.

Manganese in Ferromanganese and Steels.—The foregoing methods *a*, *b*, and *c* have all been *employed for this purpose* ; *method c* (ii) is the simplest and probably the most accurate. In method *a* it is necessary to remove iron from the solution ; this is conveniently performed by adding a slight excess of zinc oxide (*v*. J. Amer. Chem. Soc. 1902, **24**, 243 ; Ann. Chim. analyt. 1906, **11**, 124).

Manganese and Chromium occurring together in steels may be estimated by oxidising with ammonium persulphate in sulphuric acid solution in the presence of silver nitrate ; one portion of solution is titrated for total permanganate and chromate with ferrous sulphate, and another for permanganate alone by means of arsenious oxide (J. Amer. Chem. Soc. 1905, **27**, 1550 ; *v. also* Chem. News, 1901, **83**, 25 ; 1905, **91**, 3 ; Chem.-Ztg. 1905, **29**, 987 ; Bur. Stand. J. Res. *1929*, **3**, *573* ; *Chem. Zentr. 1933*, ii, 3461). For estimation of manganese in *silicate rocks*, *see* Z. anal. Chem. 1936, **105**, 81, 182.

The foregoing bismuthate method *c* (ii) may be applied in the presence of *molybdenum*, *tungsten*, *titanium* and *vanadium* ; also, with certain precautions, in the presence of *chromium* (Chem News, 1901, **84**, 247 ; Ind Eng. Chem 1912, **4**, 19). For estimation of manganese in *tungsten steels*, *v. also* J.S.C.I. 1907, **26**, 345.

Mercury.—(*a*) *By Precipitation* —Mercuric nitrate is readily titrated with $N/10$-thiocyanate, using ferric nitrate as indicator, provided that nitric acid is present in fairly high concentration (Ber. 1901, **34**, 3502 , 1902, **35**, 2015). Chloride must be absent , if necessary, the mercury is precipitated as oxide with sodium hydroxide, *and the washed precipitate dissolved in nitric* acid.

(*b*) *Iodimetrically* —The solution (O 2gHg 25–50 c.c.) containing 1 g. of potassium iodide is made alkaline with sodium hydroxide, 2–3 c c. of 40% formaldehyde are added, and the whole vigorously shaken for 2 minutes. The solution is acidified with acetic acid, and the reduced mercury is dissolved by adding an excess of $N/10$ iodine. After shaking, the excess of iodine above that required to form mercuric iodide is titrated with $N/10$ thiosulphate (Ber. 1906, **39**, 3702 ; 1907, **40**, 3276 ; Bull. Soc. chim. 1907, [iv], **1**, 1169). In other procedures, mercury is precipitated by sodium arsenite, copper or hypophosphorous acid (Z. anal. Chem. 1889, **28**, 318 ; 1898, **37**, 749 ; Analyst, 1926, **51**, 224 ; *1929*, **54**, *145*) *Mercurous salts require a preliminary* oxidation with bromine water, excess of which is removed by warming.

(*c*) *Calomel* is estimated by adding excess of concentrated hydrochloric acid and titrating with $M/40$-potassium iodate, as described on p. 658 :

$$2Hg_2Cl_2+HIO_3+5HCl \\ =ICl+3H_2O+4HgCl_2$$

If mercurous mercury is present in solution, it is precipitated as calomel by addition of sodium chloride solution in slight excess ; the precipitate is filtered off, washed with the minimum of water, and titrated as above. Mercuric solutions or solutions containing nitric acid are converted into calomel by addition of hydrochloric acid, *followed by at least a threefold* excess of ferrous sulphate, and then sodium

hydroxide in excess. The mixture is well stirred for several minutes, dilute sulphuric acid is added in excess, and the stirring is continued until the iron hydroxides have completely dissolved and white calomel remains ; this is then titrated with iodate.

(*d*) Mercuric chloride solution is titrated by potassium cyanide :

$$HgCl_2+2KCN=Hg(CN)_2+2KCl$$

Mercuric cyanide is un-ionised, so that the appearance of alkalinity, due to hydrolysis, shows the presence of the slightest excess of potassium cyanide. The mercuric solution containing sodium chloride is neutralised to bromophenol-blue, a slight excess of $N/5$-potassium cyanide is added and the excess is titrated by $N/5$-hydrochloric acid. The potassium cyanide solution, free from carbonate and hydroxide, is standardised on pure mercuric chloride (Chem.-Ztg. 1908, **32**, 1077 ; J.C.S. 1921, **119**, 1272 ; Z. anorg. Chem. 1909, **60**, 457).

(*e*) For determination of mercury by precipitation as mercuric pyridine dichromate, and titration of the dichromate, *see* Furman and State, Ind. Eng. Chem. [Anal.], 1936, **8**, 467.

Molybdenum.—(*a*) *By reduction and subsequent oxidation.* The sulphuric acid solution is reduced by passing it through a Jones Reductor (*see* p. 660) to a condition represented by the formula Mo_2O_3 ; the liquid is caught directly in ferric sulphate solution, which reoxidises the molybdenum salt, and the ferrous sulphate produced is titrated with $N/10$-permanganate (Amer. J. Sci. 1907, **24**, 313 ; *cf.* Ber. 1905, **38**, 604 ; Analyst, 1907, **32**, 250).

(*b*) *Iodimetrically.*—The solution in concentrated hydrochloric acid is boiled with a slight excess of potassium iodide until the volume is reduced to 25 c.c., when reduction to Mo_2O_5 is complete. The cold solution is diluted to 125 c.c., tartaric acid 1 g. added, then $NaOH$ until nearly neutral, followed by sodium bicarbonate and a slight excess of standard iodine. After standing in the dark for 2 hours, excess iodine is titrated by standard arsenite solution (Amer. J. Sci. 1896, **2**, 156 ; 1898, **6**, 168).

(*c*) Mo^{VI} is reduced by stannous chloride of specified acidity to Mo^{V}. Excess stannous chloride is removed by bromine and excess bromine by sodium arsenite. Mo^{V} is then oxidised to Mo^{VI} by titration with $N/10$-vanadic acid with diphenylaminesulphonic acid as indicator (Z. anal. Chem. 1936, **104**, 1).

Molybdenum in Steels and Alloys (*v.* J. Amer. Chem. Soc. 1904, **26**, 675 ; Lundell, Hoffman, and Bright, "Chemical Analysis of Iron and Steel").

Nickel.—(*a*) *By Double Cyanide Formation.*—A few drops of 10% potassium iodide are added to the cold, slightly ammoniacal nickel solution, and then a small measured volume of standard silver nitrate (3 g. of silver per litre). Standard potassium cyanide (25 g. per litre) is then run in with stirring until the precipitate of silver iodide just disappears ; more silver nitrate is added until a very faint turbidity is produced, which is then dissolved by the least possible excess of cyanide. The relative values of the silver nitrate and cyanide solutions are determined by a preliminary experiment, and the cyanide standardised against a known amount of pure nickel (or pure silver, and calculated to nickel). The method is rapid and accurate (Chem. News, 1895, **72**, 92), the complex $K_2Ni(CN)_4$ being formed quantitatively. For a modified method, *see* Bull. Soc. chim. 1936, [v], **3**, 324.

(*b*) *By Precipitation.*—The hot nickel solution containing ferric chloride (1 g.) and citric acid (2–3 g.) is made feebly ammoniacal and titrated slowly, stirring constantly, with standard potassium ferrocyanide (20 g. per litre, titrated against pure nickel), until a drop of the solution when acidified with dilute acetic acid develops a green colour in 5 minutes (J. Amer. Chem. Soc. 1910, **32**, 757 ; Bull. Soc. chim. 1907, [v], **4**, 1163).

(*c*) Nickel may also be determined by a method based on the formation of $Ni(C_5H_5N)_4(CNS)_2$: *see under* Cobalt (*d*) (p. 656).

Nickel in Steel.—Method (*b*) can be directly applied ; method (*a*) can also be employed without removing iron, molybdenum or chromium, if a sufficient excess of ammonium citrate or sodium pyrophosphate is added to the solution ; or a moderate amount (2–3 g.) of each of these reagents may be added (J. Amer. Chem. Soc. 1907, **29**, 1201 ; 1908, **30**, 1116 ; 1899, **21**, 854 ; Chem.-Ztg. 1908, **32**, 1223 ; Chem. News, 1910, **102**, 51 ; J.S.C.I. 1920, **39**, 253T). For modifications in presence of other metals, *v.* Chem. News, 1898, **78**, 177, 190 ; Johnson, "Rapid Methods for the Chemical Analysis of Special Steels, etc.," 1930. Peters (Metals and Alloys, 1935, **6**, 278) adapts method (*a*) to chromium-nickel (18:8) steels by oxidising the former metal with perchloric acid, and so preventing interference by the deep colour of chromium salts.

Niobium.—Some workers have obtained consistent results by reduction methods (Z. anorg. Chem. 1909, **62**, 383 ; Z. angew. Chem. 1933, **46**, 552), but others have found these procedures to give variable values (Analyst, 1924, **49**, 215 ; Z. anal. Chem. 1934, **99**, 398).

Nitrogen.—Ammonia (*v.* Acidimetry and Alkalimetry (p. 645)).

Hydrazine.—Hydrazine is quantitatively oxidised as follows :

$$N_2H_4+HIO_3+HCl=N_2+ICl+3H_2O$$

under the conditions given on p. 658. It may also be estimated by the slow addition of standard chloramine-T to the hydrazine solution (25 c.c.), containing sodium bicarbonate (0·5 g.), a crystal of potassium iodide and starch solution, until the blue end-point is reached :

$$N_2H_4+2CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NClNa$$
$$=N_2+2CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2+2NaCl$$

and $2HI+CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NClNa$

$$=I_2+CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2+NaCl$$

(Z. anal. Chem. 1934, **96**, 321). Standardisation of the chloramine-T can also be based on the second reaction, the chloramine-T in approximately $N/4$-hydrochloric acid, containing 1 g. of potassium iodide, being titrated with $N/10$-thiosulphate.

Hydroxylamine.—(*a*) *By Oxidation.*—(i) To a solution of hydroxylamine (about 0·05 g.),

or one of its salts, are added saturated ferric alum solution (30 c.c.) and at least 10 c.c. of 9N-sulphuric acid. The solution is boiled for 5 minutes, largely diluted with cold water, and titrated by standard permanganate or dichromate. The reaction :

$$2NH_2OH+2Fe_2(SO_4)_3 \\ =N_2O+4FeSO_4+2H_2SO_4+H_2O$$

proceeds quantitatively under the prescribed conditions (Annalen, 1887, 241, 318).

(ii) To the hydroxylamine solution are added 10–30 c.c. excess of standard ($M/60$) potassium bromate solution and then 40 c.c. of 5N-hydrochloric acid ; after 15 minutes the excess bromate is titrated by standard thiosulphate with addition of potassium iodide. Oxidation in this case is to nitric acid :

$$NH_2OH+HBrO_3=HNO_3+HBr+H_2O$$

(b) *By Reduction.*—An excess of titanous sulphate is added to the acid solution, and the ammonium salt produced is estimated by distillation with sodium hydroxide (Ber. 1909, 42, 2695).

NITRATES.—(a) *By Reduction.*—The solution is made strongly alkaline with sodium hydroxide, 5 c.c. of alcohol and 2·5–3 g. of powdered Devarda's alloy (*see* p. 598) added, and the flask connected with a distilling apparatus, the receiver of which contains excess of $N/2$-hydrochloric acid. After standing for half an hour, the liquid is steam-distilled for an equal length of time, when all the nitrate has been converted into ammonia and driven over into the acid ; the excess of the latter is then titrated (Z. anal. Chem. 1894, 33, 113 ; Analyst, 1910, 35, 307 ; *v.* also the Gravimetric Section (p. 598)). It is stated (Analyst, 1936, 61, 249) that the amount of sodium hydroxide recommended by Devarda is excessive and leads to inaccurate results. The optimum quantities are nitrate (1 g.), Devarda's alloy (3 g.), sodium hydroxide (2 g.), and water (250 c.c.). Nitrates, *e.g.* in fertilisers, may be determined by conversion into ammonia by treatment with iron (reduced by hydrogen) in presence of sulphuric acid. Ammonia is distilled after addition of sodium hydroxide in excess (*see* "Fertilisers and Feeding Stuffs Regulations," 1932).

(b) *By Oxidation of Ferrous Salts.*—Reaction, in an inert atmosphere, proceeds according to the equation :

$$3FeCl_2+HNO_3+3HCl \\ =3FeCl_3+NO+2H_2O$$

The nitrate (0.25 g.) is placed in a long-necked flask, fitted with inlet and outlet tubes for carbon dioxide, and air is expelled by the gas. A solution containing a known weight of ferrous ammonium sulphate (approximately 10 g.) and about 40 c.c. of concentrated hydrochloric acid are added. The reactants are heated gently for 10 minutes and then boiled until the dark red colour changes completely to yellow-brown. The liquid is cooled with the stream of carbon dioxide still flowing, then diluted considerably with water and titrated by $N/2$-dichromate, after addition of phosphoric acid and barium diphenylaminesulphonate (*see* p. 647). A smaller excess of ferrous iron can be used in presence of molybdic acid as catalyst (J. Amer. Chem. Soc. 1933, 55, 1454 ; Z. anal. Chem. 1877, 16, 267). The foregoing method cannot be used in presence of organic matter ; in such cases the nitric oxide evolved is determined (Z. anal. Chem. 1884, 23, 151 ; J.C.S. 1880, 37, 468 ; 1882, 41, 345).

NITRITES.—(a) *By Oxidation.*—The nitrite solution is slowly added to a measured quantity of $N/10$-permanganate, which is acidified with sulphuric acid, diluted to 400 c.c., and warmed to 40°C., until the colour is just discharged : $2HNO_2 \equiv O_2$. Reaction is slow towards the end. Alternatively, the nitrite is added to excess of acidified permanganate and, after the mixture has stood for 15 minutes, the excess of permanganate is determined by ferrous sulphate or oxalic acid (*see* J. Amer. Chem. Soc. 1919, 41, 524 ; Ind. Eng. Chem. [Anal.], 1933, 5, 112).

(b) *Iodimetrically.*—Several methods have been based on the reaction

$$2HI+2HNO_2=I_2+2NO+2H_2O.$$

It is necessary to perform the experiment in an atmosphere free from oxygen ; the iodine may be determined by thiosulphate or arsenite. (For details, *v.* Pharm. J. 1889, 19, 741 ; Chem News, 1904, 90, 114 ; Analyst, 1934, 59, 99 ; *cf.* ORGANIC ANALYSIS, Aromatic amines (p 627).)

(c) *By Chloramine-T.*—To a known volume (excess) of chloramine-T solution, acidified by dilute acetic acid, is added a measured volume of nitrite solution :

$$CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NClNa+HNO_2+H_2O \\ =CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2+HNO_3+NaCl$$

After a few minutes, excess chloramine is titrated as in its standardisation (*see* p. 663) (Pharm. Weekblad, 1926, 63, 1117).

Osmium.—*Iodimetrically.*—The solution of osmium tetroxide, acidified by sulphuric acid, is treated with an excess of potassium iodide, and then titrated with $N/10$ thiosulphate, with starch iodide paper as external indicator : $OsO_4+4HI=OsO_2+2H_2O+2I_2$ (Chem. Zentr. 1898, ii, 65 ; Z. anorg. Chem. 1910, 65, 429).

Oxygen.—PEROXIDES.—(a) *Iodimetrically.*—Such peroxides as those of manganese and lead may be estimated by *Bunsen's method* (*see* p. 657). Finely divided peroxides of manganese react quantitatively with cold dilute hydrochloric acid or phosphoric acid, and potassium iodide (J.C.S. 1880, 37, 128), a method of estimation that is available with the peroxides of the alkali and alkaline-earth metals, which do not give satisfactory results by the distillation method (Arch. Pharm. 1902, 240, 437). Hydrogen peroxide may be determined in this manner (Analyst, 1888, 13, 62), but reaction is slow ; it becomes almost instantaneous in presence of a few drops of ammonium molybdate (Pharm. Weekblad, 1919, 56, 949). Interference of stabilisers is minimised by addition of 0.5 g. of pyrogallol (J. Assoc. Off. Agric. Chem. 1933, 16, 395).

(b) *By Reduction.*—Hydrogen peroxide, or peroxides of the alkali and alkaline-earth metals, may be dissolved in cold dilute acid and titrated with $N/10$-permanganate, which loses as much

oxygen as is lost by the peroxide (*v.* also Gas-Volumetric Methods). Unlike method (*a*), above, this method cannot be used in presence of many organic substances (p. 688).

Peracids.—*Perborates* are determined as described in (*a*) above. For the determination of perborates in soaps, *see* Analyst, 1920, **45**, 88; Z. anal. Chem. 1933, **92**, 95. *Percarbonates* are estimated as in method (*b*), decomposition by acid occupying about 30 minutes. *Perdisulphates* are determined by dissolving in an excess of standard ferrous ammonium sulphate solution in an atmosphere of carbon dioxide, 100 c.c. of water at about 90°C. are added and, after 1 minute, the solution is cooled and excess ferrous iron is titrated by standard permanganate. Hydrogen peroxide and Caro's acid (permonosulphuric acid) react similarly; for the estimation of each in admixture, *see* Analyst, 1933, **58**, 464; Z. anorg. Chem. 1931, **195**, 61.

Palladium.—A palladous solution is precipitated by a known amount of salicylaldoxime as $Pd(C_7H_6O_2N)_2$. Excess salicylaldoxime in the filtrate is estimated by boiling with ferric sulphate solution and titrating the ferrous iron by permanganate (Bull. Soc. chim. Belg. 1936, **45**, 9), the oxime being hydrolysed to hydroxylamine (*q.v.*).

Phosphorus.—Phosphoric Acid (Ortho-).—(*a*) (*v.* Acidimetry and Alkalimetry, p. 645).

(*b*) *Acidimetrically, with Previous Precipitation.*—The precipitate of ammonium phosphomolybdate $(NH_4)_3PO_4,12MoO_3$ (*v.* Gravimetric section, p. 598) after washing with water is dissolved in a slight excess of standard potassium or sodium hydroxide free from carbonate, and the excess titrated with standard nitric acid, using phenolphthalein as indicator. As the ammonia is not boiled off, one molecular proportion of P_2O_5 requires 23 molecules of K_2O (J. Amer. Chem. Soc. 1895, **17**, 950; 1897, **19**, 703; J.S.C.I. 1904, **23**, 1186). In other procedures, the ammonia is boiled off and $P_2O_5=26K_2O$ (Analyst, 1924, **49**, 565).

(*c*) *By Precipitation.*—The solution, feebly acid with acetic acid, containing 5 c.c. of sodium acetate solution (100 g. of sodium acetate and 50 c.c. of glacial acetic acid per litre), is heated to 90°–100°C. and standard uranium acetate solution (35 g. per litre) is run in from a burette until a drop of the solution gives a brown coloration with potassium ferrocyanide upon a white tile. The compound formed is uranyl ammonium phosphate, $(UO_2)NH_4PO_4$. In analysing alkali phosphates, the uranium solution is standardised against pure potassium dihydrogen phosphate, while a solution of calcium phosphate in acetic acid, standardised gravimetrically by the method of Woy (Chem.-Ztg. 1897, **21**, 442), must be used if the uranium acetate is to be used for estimating phosphates of the alkaline earths (J.S.C.I. 1892, **11**, 328). It is essential that titrations should be made under conditions closely approximating to those which obtained when the uranium solution was standardised.

Phosphorus in Iron and Steel.—This is usually separated as ammonium phosphomolybdate; it may then be titrated according to *b* above, or the precipitate is washed with dilute ammonium sulphate, dissolved in ammonia, the solution strongly acidified with sulphuric acid, and determined after reduction to Mo_2O_3 as described under *Molybdenum*, p. 605 (Scott "Standard Methods of Chemical Analysis," 1926; Blair, "Analysis of Iron").

Phosphorus, Elemental.—The material containing phosphorus (about 0·1 g.) is weighed into a flask containing 2 c.c. of carbon tetrachloride; 20 c.c. of 5% potassium iodate and 50 c.c. of *N*-sulphuric acid are added. The flask is attached to a ground-in condenser and the mixture is refluxed for 4 hours to complete the reaction:

$$2P+2HIO_3+2H_2O=2H_3PO_4+I_2$$

The iodine is then distilled into excess of potassium iodide and titrated by *N*/10-thiosulphate. Iodate remaining can also be determined in an aliquot portion of the solution left in the distillation flask (J. Amer. Chem. Soc. 1927, **49**, 9).

Phosphorous Acid.—To the phosphite solution (10 c.c.), containing about 0·1 g. of the salt, are added 0·5 g. of sodium bicarbonate and 20 c.c. of *N*/10-iodine. After 2 hours, 10 c.c. of 10% acetic acid are added and the excess iodine is titrated. The reaction is

$$H_3PO_3+I_2+H_2O=H_3PO_4+2HI$$

Hypophosphorous Acid.—To the solution (10 c.c.) in a stoppered flask, containing about 0·1 g. of the salt, are added 10 c.c. of 25% sulphuric acid and 30 c.c. of *N*/10-iodine solution. The mixture is left in the dark for 10 hours and excess iodine is then titrated. Oxidation proceeds only to phosphorous acid:

$$H_3PO_2+I_2+H_2O=H_3PO_3+2HI:$$

but further oxidation in presence of bicarbonate can then be effected to phosphoric acid (*see* Phosphorous Acid); the procedure can be used for the analysis of mixtures of phosphites and hypophosphites.

Platinum may be determined by adding a chloroplatinate solution to excess of potassium iodide solution and titrating the liberated iodine:

$$PtCl_4+4KI=PtI_2+4KCl+I_2$$

Auric solutions (*see* p. 657) are also reduced.

Potassium is precipitated as $K_2NaCo(NO_2)$. Various descriptions are published, which must be closely followed to obtain a precipitate of this composition (J.C.S. 1900, **77**, 1076; Analyst, 1923, **48**, 250; 1926, **51**, 450; Amer. J. Sci. 1907, **24**, 433; J. Assoc. Off. Agric. Chem. 1933, **16**, 137; Ind. Eng. Chem. [Anal.], 1933, **5**, 163; J.S.C.I. 1934, **53**, 392; Analyst, 1935, **60**, 677). Nitrite is then determined by permanganate (*cf.* p. 664) or by ceric sulphate, and since Co^{III} is converted to Co^{II}, $2K_2NaCo(NO_2)_6=11O$.

Rhenium.—*See* Chem. News, 1932, **145**, 186; Z. anorg. Chem. 1935, **222**, 56.

Selenium.—Selenious Acid.—(*a*) *By Oxidation.*—The solution containing about 0·1 g. of selenious acid in 25 c.c. of 40% sulphuric acid is diluted to 150 c.c. and oxidised by excess (at least 10 c.c.) of *N*/10-potassium permanganate, after addition of sodium phosphate (12 g.) to

prevent precipitation of manganese dioxide. After 30 minutes, excess permanganate is titrated by ferrous sulphate:

$$H_2SeO_3+O=H_2SeO_4$$

(J. Amer. Chem. Soc. 1926, 48, 2550).

(*b*) *Iodimetrically.*—The solution (100 c.c.) containing about 0·1 g. of selenious acid in a stoppered bottle is treated with 10 c.c. of 25% hydrochloric acid, 20 c.c. of carbon disulphide (to prevent adsorption of iodine on selenium), and 10 c.c. of 10% potassium iodide, added in a fine stream. The mixture is shaken for 1 minute, and the liberated iodine is titrated by thiosulphate:

$$H_2SeO_3+4HI=Se+2I_2+3H_2O$$

(Chem.-Ztg. 1928, 52, 142). 15 c.c. of 2% starch, which acts as a protective colloid and prevents precipitation of selenium, can be used instead of carbon disulphide (Chem. Weekblad, 1934, 31, 333).

Small quantities of selenium in sulphur are determined by combustion to dioxides in oxygen; the resulting solid selenium dioxide is estimated iodimetrically (Ind. Eng. Chem. [Anal.], 1935, 7, 423).

SELENIUM AND SELENIC ACID.—The powdered element (about 4 g.) is suspended in 100 c.c. of water and warmed with potassium bromate (10 g.). The resulting solution of selenic acid is cooled and diluted to 1 litre. To 20 c.c. of this solution are added 20 c.c. of 2*M*-potassium bromide and 10 c.c. of hydrochloric acid, and the solution is heated to effect reduction to selenious acid, which is then titrated as above (Chem. Weekblad, 1934, 31, 333).

Silver.—*By Precipitation.*—(i) The nitric acid solution is titrated with standard sodium chloride until no further precipitation is observed (For details of this very exact method, *v.* ASSAYING.) A number of devices have been described for rapidly filtering a portion of the liquid in order to test for further precipitation (J.C.S. 1908, 93, 1037; Gazzetta, 1909, 39, ii, 240). A modified method consists in adding a slight deficit of sodium chloride, filtering, and titrating the remaining silver with dilute ammonium thiocyanate (J. Amer. Chem. Soc. 1897, 19, 814; *v. also* J.C.S. 1900, 77, 232; Z. angew. Chem. 1904, 17, 647). (ii) Titration may be effected with *N*/10-thiocyanate as described under PREPARATION OF STANDARD SOLUTIONS, p. 649. (iii) Various procedures in which adsorption indicators are used are described under Preparation of Standard Solutions and Estimation of Halogens in Halide Salts, p. 659.

Sodium.—(i) The precipitate,

$$NaZn(UO_2)_3(C_2H_3O_2)_9$$

or

$$NaNi(UO_2)_3(C_2H_3O_2)_9$$

(*see* GRAVIMETRIC SECTION, p. 607), is dissolved, and uranium (*q.v.*) is estimated by reduction or by titration with standard phosphate solution *see* Phosphoric Acid, p. 665) (J. Amer. Chem. Soc. 1930, 52, 1349). (ii) For method based on precipitation of Na_2HSbO_4, but requiring use of a correction factor, *see* Z. anal. Chem. 1936, 104, 406.

Sodium and Potassium.—If these two alkali metals are present together as chloride, and no other salts are present except those of ammonium, the solution is evaporated to dryness, gently ignited, until free from ammonium salts and moisture (which is rather tenaciously retained), and weighed, the weight being *w* g. The mixed chlorides are then dissolved in water, and the chlorine determined by means of silver nitrate; if *c* is the weight of chlorine thus found, then

$$KCl=3\cdot6303(2\cdot1026c-w)$$

and $$NaCl=w-KCl$$

Sulphur, Acids of.—HYDROGEN SULPHIDE.—*Iodimetrically.*—(i) The gas or a measured volume of solution is absorbed in an excess of *N*/10 iodine, the excess being afterwards titrated with *N*/10-thiosulphate: $H_2S=I_2$. Direct titration with iodine leads to low results (Z. anal. Chem. 1906, 45, 541). (ii) To a measured volume of *N*/10 arsenious acid are added 20 c.c. of hydrogen sulphide water, and the mixture is acidified by hydrochloric acid. The arsenious sulphide

$$(As_2O_3+3H_2S=As_2S_3+3H_2O)$$

is filtered off and washed, and the excess of arsenite is determined in an aliquot portion of the filtrate by titration with iodine.

For the determination of sulphur in sulphides decomposable by acids to yield hydrogen sulphide, *see* Fox and Bowles, "The Analysis of Paints, Pigments, and Varnishes," 1927, p. 33, Analyst, 1933, 58, 682. For the determination of sulphur in pyrites, ores, etc., *see* J.S.C.I. 1888, 7, 305; Z. anal. Chem. 1907, 46, 9. For the determination of *Polysulphides*, *see* Z. anorg. Chem. 1925, 142, 115.

HYPOSULPHUROUS ACID,[1] $H_2S_2O_4$.—Hibbert and Knecht (Ber. 1907, 40, 3819) employed a volumetric process based on the use of methylene blue and titanous chloride, and this method is still utilised. Ammoniacal silver nitrate can be used as follows (J. Amer. Chem. Soc. 1921, 43, 1307; Bull. Soc. chim. 1906, 35, 293). About 0·5 g. of dry hyposulphite is treated with a twofold excess of aqueous silver nitrate containing much more than sufficient ammonia to redissolve the silver oxide first precipitated. In dissolving in this reagent, hyposulphite is forthwith oxidised to sulphite, precipitating elemental silver, which is collected on asbestos and washed with dilute ammonia containing ammonium nitrate, the latter being added to prevent the finely divided silver from passing through the filter. The silver is then dissolved in nitric acid, and after boiling off nitrous fumes, the solution is titrated with *N*/10 thiocyanate, using ferric alum as indicator.

For the estimation of hyposulphite in presence of sulphite, *see* Giorn. Chim. Ind. Appl. 1921, 3, 501; Chem. and Ind. 1923, 42, 290; Col. Trade J. 1924, 14, 180; and in presence also of thiosulphate, *see* Z. anal. Chem. 1930, 80, 1.

SULPHUROUS ACID.—(*a*) *Iodimetrically.*—Sulphurous acid is estimated by running it into dilute standard iodine solution, acidified by

[1] Sometimes erroneously called hydrosulphurous acid

hydrochloric or sulphuric acid, with constant stirring until the colour of the iodine is discharged :

$$H_2SO_3+I_2+H_2O=H_2SO_4+2HI$$

Titration cannot be carried out in the reverse direction, as side reactions then take place. Sulphites may be determined by adding the powdered salt to excess of $N/10$-iodine, and after decomposition is complete titrating back with $N/10$-thiosulphate.

(*b*) *By Potassium Iodate.*—The reaction

$$2SO_2+H_2O+2HCl+KIO_3 \\ =ICl+KCl+2H_2SO_4$$

takes place under conditions described on p. 658. The method can be used for estimating sulphur dioxide in wines by distilling off sulphur dioxide after addition of phosphoric or tartaric acid, and collecting the gas in dilute alkali-containing glycerol to prevent atmospheric oxidation of the sulphite.

SULPHURIC ACID.—(*a*) *Iodimetrically.*—The feebly acid boiling dilute sulphate solution is precipitated with an excess of a solution of barium chromate in hydrochloric acid (3–4 g. $BaCrO_4$, 30 c.c. conc. HCl, diluted to 1 litre). Barium sulphate is thus precipitated, and an equivalent of chromic acid liberated. The boiling solution is neutralised with powdered chalk to remove excess of barium chromate, and the chromic acid in the cold filtrate titrated iodimetrically : $CrO_3=SO_3$ (Amer. Chem. J. 1889, **11**, 567 ; Chem.-Ztg. 1898, **22**, 357).

(*b*) *By Precipitation.*—(i) *By titration with barium chloride* with rhodizonic acid as indicator (*see* Barium and 1934, A. 500 ; Z. anal. Chem. 1936, **105**, 346). (ii) *By use of benzidine.*—The sulphate is precipitated from dilute solution as benzidine sulphate by means of excess of benzidine hydrochloride solution. The precipitate is suspended in water, heated to 50°C., and titrated by $N/10$-sodium hydroxide with phenolphthalein as indicator. When the titration is almost finished, the liquid is boiled for 5 minutes, and the titration then completed: $2NaOH=H_2SO_4$ (Z. angew. Chem. 1907, **20**, 9). (iii) A fairly accurate titration can be effected by lead nitrate with eosin as adsorption indicator (Ind. Eng. Chem. [Anal.], 1936, **8**, 130).

THIOSULPHURIC ACID.—*Iodimetrically.*—Thiosulphates are titrated with iodine as in standardising thiosulphate solution (*see* p. 648) ; sparingly soluble salts are suspended in water in a stoppered bottle and shaken vigorously throughout the titration.

PERSULPHURIC ACID.—*See* p. 665.

DITHIONIC ACID.—Dithionic acid is quantitatively oxidised to sulphuric acid by boiling for 1 hour with potassium dichromate, strongly acidified by sulphuric acid. Unchanged dichromate is then determined iodimetrically. Sulphurous acid, if present, is first removed by boiling with $N/2$-acetic acid for 15 minutes (J.C.S. 1933, 5).

POLYTHIONIC ACIDS.—*See* Z. anorg. Chem. 1925, **142**, 119 ; 1927, **166**, 177 ; J.C.S. 1927, 1451, for the estimation of tri-, tetra-, and penta-thionates, both alone and if mixed with bisulphites and thiosulphates.

SULPHUR, ELEMENTAL.—Sulphur (0·1 g.) is converted into sodium thiosulphate by boiling under reflux for 30 minutes with sodium sulphite (2 g.), water (30 c.c.), and soft paraffin (1 g.). The solution is cooled and poured off from the paraffin, which is washed with hot water, followed by cooling. To the combined solutions are added formalin (10 c.c.), to render sulphite inactive, 20% acetic acid (20 c.c.), and water to a total volume of 150 c.c. ; thiosulphate is then titrated by iodine (Quart. J. Pharm. 1934, **7**, 179). For a method depending upon the conversion of sulphur into thiocyanate, *see ibid.* 1933, **6**, 431 ; Z. anal. Chem. 1932, **91**, 32. For determination of sulphur in presence of selenium, *see* Z. anal. Chem. 1935, **102**, 353. For the estimation of free sulphur in rubber, *see* J.S.C.I. 1933, **52**, 296T ; Ind. Eng. Chem. [Anal.], 1935, **7**, 103.

Tellurium.—TELLUROUS ACID.—*By Oxidation.*—(i) The solution is oxidised by permanganate, exactly as described under Selenious Acid, p. 665. (ii) The solution (200 c.c.), containing 15 c.c. of concentrated hydrochloric acid and a measured excess of $N/10$-dichromate, is allowed to stand for 30 minutes. Excess of dichromate is then determined. Selenious acid is not oxidised (J. Amer. Chem. Soc. 1923, **45**, 1423).

TELLURIC ACID.—*Iodimetrically.*—The tellurate is distilled with hydrobromic acid in Bunsen's apparatus (*see* p. 657), the bromine is absorbed in potassium iodide and the iodine set free is titrated with $N/10$-thiosulphate. Tellurium trioxide must be previously dissolved in concentrated potassium (not sodium) hydroxide, since it is scarcely attacked by hydrobromic acid. The reduction proceeds to tellurous acid (Z. anorg. Chem. 1894, **7**, 132 ; Monatsh. 1923, **44**, 349).

Thallium.—Thallous salts are oxidised to thallic compounds by potassium iodate or by chloramine-T in presence of $5N$-hydrochloric acid, under the conditions described on p. 658. The reaction is

$$2TlCl+HIO_3+5HCl=2TlCl_3+3H_2O+ICl$$

(Analyst, 1926, **51**, 137 ; 1934, **59**, 736 ; J. Amer. Chem. Soc. 1936, **58**, 113).

Oxidation can also be carried out by potassium bromate, or by chloramine-T and potassium bromide, with methyl orange as indicator, as described under Antimony (*see also* Z. anorg. Chem. 1926, **153**, 276 ; Analyst, 1934, **59**, 736).

Thorium.—$Th(C_9H_6ON)_4, C_9H_7ON$ is precipitated by oxine (Z. anal. Chem. 1935, **100**, 98 ; Monatsh. 1929, **53**, 596), and determined bromometrically (*see* p. 650).

Tin.—STANNOUS SALTS.—(*a*) *Iodimetrically.*—The cold hydrochloric acid solution of the stannous salt is titrated with $N/10$-iodine : $Sn=I_2$; the solution should contain 25–40% by volume of concentrated acid. Exposure of the solution to air must be avoided, since stannous salts readily undergo oxidation ; it is preferable to work in an atmosphere of carbon dioxide and to remove air from the iodine solutions used in the titrations (Okell, Analyst, 1935, **60**, 803). Many metals, including arsenic and antimony, are without effect.

(*b*) *By Chloramine-T.*—The concentration of acid must not exceed 5%; starch and a crystal of potassium iodide are added, and the solution *is titrated by N/10 chloramine-T* (*see* p. 663).

STANNIC SALTS.—Before titration with iodine, stannic salts must be reduced; this may be accomplished by heating the hydrochloric acid solution with iron, nickel, zinc, antimony, or lead foil (Chem. News, 1901, 84, 167; J.S.C.I. 1916, 35, 1087T; 1918, 37, 287T; Pharm. Weekblad, *1917, 54, 718; 1919, 56, 1466*); hypophosphorous acid has also been used (Analyst, 1931, 56, 171).

For the determination of tin in ores and alloys, *see* Chem. News, 1877, 36, 238; 1901, 84, 167; Chem. and Ind. 1934, 53, 615.

For separation of tin from arsenic and antimony, *see* p. 652.

Titanium.—*By Reduction and Subsequent Oxidation.*—It is difficult to obtain accurate results with quantities of titanium dioxide exceeding 0·15 g. The warm, dilute sulphuric acid solution of titanic salt is reduced to the tervalent condition in a Jones Reductor (*see* p. 660) and delivered into ferric sulphate solution (*see* Molybdenum p. 663), ; the equivalent quantity of ferrous sulphate produced is titrated with $N/10$-permanganate or -dichromate.

Titanium in titanium-pigments may be determined by dissolving the material in concentrated sulphuric acid and ammonium sulphate. The solution is reduced by liquid zinc amalgam, potassium thiocyanate is added as indicator and titration is carried out with standard ferric alum solution (Ind. Eng. Chem. [Anal.], 1936, 8, 48; Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," 1925).

Titanium and Iron (*see* IRON, *p. 661; cf. also* J. Amer. Chem. Soc. 1895, 17, 878).

Tungsten.—*By Reduction and Subsequent Oxidation.*—The reduction by zinc and hydrochloric acid leads to variable results (*cf.* Ind. Eng. Chem. [Anal.], 1934, 6, 476). It is claimed that, by reduction with lead amalgam, tungstate is reduced exactly to W_2O_3, whereas with bismuth amalgam, reduction proceeds to W_2O_5 (Z. anorg. Chem. 1927, 163, 206).

Uranium.—(*a*) *By Reduction and Subsequent Oxidation.*—The solution is reduced by passage through a Jones Reductor (*see* p. 660). Reduction proceeds a little too far, but oxidation to the uranous state (U^{IV}) is accomplished by bubbling air through the solution for a few minutes until the dingy green colour changes to a bright green. The solution is titrated by $N/10$-permanganate or -dichromate (J. Amer. Chem. Soc. 1925, 47, 2637), in the latter titration, 2% ferric chloride solution (25 c.c.) can be added to accelerate the colour change of the diphenylaminesulphonic acid used as indicator (J. Amer. Chem. Soc. 1933, 55, 1871).

(*b*) *By Oxine.*—Uranium is precipitated as $UO_2(C_9H_6ON)_2,C_9H_7ON$ (Monatsh. 1929, 53, 596) and determined bromometrically (*see* p 650)

(*c*) *Separation from Iron and Aluminium.*—The acid solution, containing ammonium salts, is mixed with an excess of ammonium carbonate and sulphide in a closed flask. The precipitate contains the iron and aluminium, and the uranium remains in solution as the double carbonate $(UO_2)CO_3,2(NH_4)_2CO_3$. The filtrate is concentrated considerably, acidified with hydrochloric acid, the CO_2 boiled off, and the *uranium precipitated as* $(NH_4)_2U_2O_7$ *by* addition of ammonia. The precipitate is heated at 170°C. with dilute sulphuric acid in an atmosphere of carbon dioxide, and the cooled solution is titrated by $N/10$-permanganate. One third of the uranium is thereby reduced to the quadrivalent state, whence 1 c.c. of permanganate= 0·03588 g. *U*.

Uranium and Vanadium (*v.* J. Amer. Chem. Soc. 1906, 28, 1443).

For the determination of uranium in ores, *see* J. Amer. Chem. Soc. 1934, 56, 277.

Vanadium.—(*a*) *By Reduction and Subsequent Oxidation.*—(i) The vanadic solution containing sulphuric acid is boiled with sulphur dioxide until the colour is a pure blue, and the excess of sulphur dioxide then expelled with carbon dioxide; the solution, containing vanadium salt corresponding to the oxide V_2O_4, is then titrated hot with $N/10$ permanganate. Molybdic acid or uranyl salts are not reduced under these conditions. (ii) The sulphuric acid solution is passed through a Jones Reductor (*see* p. 660) and the reduced solution collected and titrated as described under Molybdenum. In this case reduction proceeds as far as the oxide V_2O_2 (Amer. J. Sci. 1908, 25, 332; *cf. ibid.* 1903, 15, 389). (iii) V_2O_2 *is oxidised* quantitatively to V_2O_3 by Lang's iodine cyanide method described on p. 658 (Analyst, 1934, 59, 736).

(*b*) *Iodimetrically.*—To 50 c.c. of approximately $M/30$-vanadate solution, 2 c.c. of concentrated sulphuric acid are added and the solution is boiled in a 400 c.c. conical flask in a *stream of carbon dioxide. The inlet tube should* reach to about 1 cm. above the surface of the liquid and the outlet tube should dip under water. Carbon dioxide is passed through continuously, and the flask is cooled to room temperature. Solid potassium iodide (3 g.) is quickly added, the rate of flow of gas is reduced so that iodine is not lost

$$(V_2O_5+2HI=V_2O_4+H_2O+I_2),$$

and after shaking gently for 2 minutes, the solution is diluted to about 300 c.c. with cold, boiled-out, distilled water, and titrated by $N/10$ thiosulphate in presence of starch (J. Amer. Chem. Soc. 1927, 49, 1138; *see also ibid.* 1929, 51, 1366).

Vanadium and Chromium (*v.* Bull. Soc. chim. 1904 [iii], 38, 962; Amer. J. Sci. 1908, 26, 333; Analyst, 1928, 53, 475). For rapid method of determination in steels, *see* Ind. Eng. Chem. [Anal.], 1933, 5, 158.

Vanadium and Uranium.—Since uranyl salts are not reduced by sulphur dioxide, vanadium can be determined in presence of uranium by method (*a*) (i) (*see also* J. Amer. Chem. Soc. 1906, 28, 1443).

Vanadium and Iron.—See under Iron, p. 661; *also* J. Amer. Chem. Soc. 1908, 30, 1229, 1233).

Vanadium and Molybdenum.—See Amer. J. Sci. 1908, 25, 332, and also method (*a*) (i) above.

Zinc.—(*a*) *By Potassium Ferrocyanide.*—(i) The chloride solution, containing 3 c.c. of concentrated hydrochloric acid in 250 c.c., is

heated nearly to boiling, and titrated with $M/20$-potassium ferrocyanide solution (21·11 g. per litre, standardised against pure zinc) until one or two drops of the solution produce a brown coloration with a drop of a strong solution of uranium nitrate (J. Amer. Chem. Soc. 1900, **22**, 198 ; 1904, **26**, 4 ; 1908, **30**, 25) or ammonium molybdate (Chem.-Ztg. 1905, **29**, 951 ; J.S.C.I. 1909, **28**, 1138) solution, the latter being the more sensitive.

(ii) The method is greatly improved by use of an internal indicator (J. Amer. Chem. Soc. 1927, **49**, 356). The solution, 100 c.c. containing 0·10–0·15 g. of zinc, 5 c.c. of concentrated sulphuric acid, 10 g. of ammonium chloride or sulphate, and three drops of 1% diphenylbenzidine solution in concentrated sulphuric acid, is titrated by $M/20$-potassium ferrocyanide solution containing a little ferricyanide (0·2 g. per litre). The solution soon acquires a blue-violet coloration, which changes sharply to a pale green at the end-point. The precipitate having the composition $K_2Zn_3[Fe(CN)_6]_2$, 3 atoms of Zn=2 mols. of ferrocyanide. With small quantities of zinc the colour may be slow in appearing, but addition of some of the liquid and suspension resulting from an accurately completed titration will bring this about. This elegant method is not always reliable, but deserves further investigation.

(b) *By Oxine.*—Zinc is precipitated as $Zn(C_9H_6ON)_2$ and determined bromometrically (*see* p. 650). Separation from magnesium is effected both from tartrate and from acetate solutions (Z. anal. Chem. 1927, **71**, 122, 225 ; Analyst, 1933, **58**, 388).

For determination of zinc in ores and alloys, *see* J. Amer. Chem. Soc. 1907, **29**, 205 ; Chem.-Ztg. 1905, **29**, 951 ; J.S.C.I. 1905, **24**, 228, 1278.

For determination in zinc dust, *see* Z. anal. Chem. 1890, **29**, 253.

For determination of zinc in foods, *see* Sylvester and Hughes, Analyst, 1936, **61**, 734.

Zirconium.—*By Oxine.*—Zirconium is precipitated as $Zr(C_9H_6ON)_4$ in absence of chloride, and determined volumetrically (*see* p. 650) (Z. anal. Chem. 1935, **101**, 101).

A. D. M. and A. M. W.

COLORIMETRIC ANALYSIS.

Methods for the Determination of Metals and Acid Radicals.

The principle of colorimetric analysis consists in the formation of highly coloured substances resulting from the action of chosen reagents. It sometimes happens that, within certain limits, the intensity of the colour produced is a linear function of the concentration of the substance which is being determined ; this, however, does not always obtain and it is then necessary either to prepare standards which exactly balance the actual test or to construct a curve showing the relation between the intensity of the colour and the amount of the substance giving rise to it. In discussing the colorimetric determination of lead by the sulphide method, Warington (J.S.C.I. 1893, **12**, 97) stressed the importance of making comparisons with standards containing the same quantity of dissolved salts as are present in the solution under examination. Later, it was shown by Hill (Chem. and Druggist, 1905, **77**, 388) that "the colour given by a definite quantity of lead sulphide in a solution of any given salt is sensibly the same for different concentrations of the salt, provided that the concentrations vary between certain limits." Hence, in determining lead present as an impurity in soluble colourless salts, it is now customary to treat a solution containing 7 or 12 g. of the salt under examination with the appropriate reagents and to match the resulting colour against a series of standards similarly prepared and each containing 2 g. of the same substance. The degree of accuracy attainable by colorimetric methods approximates to about ±5%, which, having regard to the extreme sensitivity of many of the reactions, is generally amply sufficient for most purposes.

Many instruments (colorimeters) are available for measuring the colours produced by chemical reactions. Quite apart from these, a novel and useful apparatus known as the B.D.H. Lovibond Nesseleriser has recently been introduced which is of special interest in colorimetric analysis (*see* p. 670). It consists essentially of a bakelite case for holding vertically two Nessler glasses between a reflector and a detachable rotating disc having nine apertures containing a series of graded permanent glass colour standards. Each disc constitutes a series of ready-made standards designed for one particular test conducted under specified conditions. Discs are available to suit many of the colorimetric methods in common use, and the manufacturers are continually extending the range.

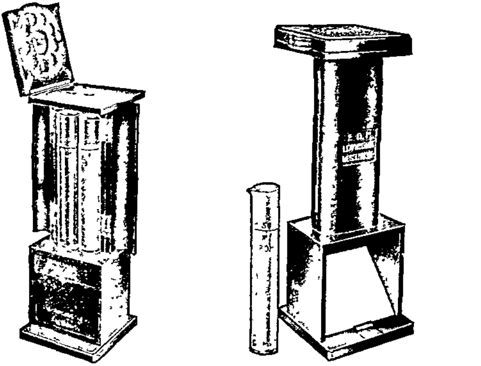
Colorimetric analysis finds its widest application in biochemical work where the determination of minute quantities of constituent substances is of great importance. Limitations of space preclude any description of these methods here, but many colorimetric processes are described under separate headings, *e.g.* the determination of ammonia and of nitrites in water. In this article only those metals and acid radicals are mentioned for which satisfactory methods are at present available. Finally, it may be observed that the principles of colorimetry have been applied to the determination of the most widely diverse substances ; *e.g.* reducing sugars, vitamin-*A*, cholesterol, bilirubin, vegetable alkaloids, and also rancidity in fats. The technique for many of these tests is described under the appropriate heading.

METALS.

Aluminium.—The ammonium salt of aurine tricarboxylic acid, proposed by Hammett and Sottery (J. Amer. Chem. Soc. 1925, **47**, 142) as a qualitative test, has been applied as a reagent for quantitative work by Lampitt and Sylvester (Analyst, 1932, **57**, 418). For the determination, 5 c.c. of the neutral solution under test, containing not more than 0·06 mg. of Al are mixed in a flask with 2 c.c. of $5N$-HCl, 5 c.c. of $5N$-ammonium acetate, 20 c.c. of 50% (by volume) aqueous solution of glycerol and 5 c.c. of a 0·2% aqueous solution of the reagent. The flask is immersed in boiling water for 5 minutes, then

cooled in ice water for 5 minutes and the contents transferred to a 50 c.c. graduated flask containing 3 c.c of ammonia-ammonium carbonate solution made by mixing equal volumes of 10N-ammonium hydroxide and 2N-ammonium carbonate. After dilution to the mark, the colour of the solution is measured in a Lovibond tintometer using a ½-in. cell. The measurement must be made exactly 5 minutes after mixing with the ammonia-ammonium carbonate solution The Al content of the solution is derived from the expression $(R-0\ 55)\times 11\ 5\times 10^{-6}$ g., where R is the value of the red component in Lovibond units. This method, although complicated, is probably the best yet available

Antimony.—A method using potassium iodide and pyridine has been proposed by Clarke (Analyst, 1928, 53, 373) and is applied to the determination of antimony present as impurity in tin. The preliminary separation is effected by Reinsch's reaction, the antimony being finally dissolved in 20 c.c. of 25% (by volume) sulphuric acid. Into a 100 c c. Nessler glass, 10 c.c. of 1% gum arabic, 5 c.c. of 20% potassium iodide, 1 c.c. of 10% aqueous pyridine, 1 c.c. of sulphur dioxide solution (1/10 saturated) and 60 c.c. of dilute (1 3) sulphuric acid and the solution of antimony are added successively. A standard antimony solution (made by dissolving tartar emetic in 10% sulphuric acid and containing 0·1 mg. Sb per c.c.) is run into another Nessler



The B.D H. Lovibond Nesslerıser manufactured by The Tintometer, Ltd , *Salisbury, in association with The British Drug Houses, Ltd , London, N.1.*

glass containing similar quantities of reagents (except that 80 c.c. of 1·3 sulphuric acid are used in place of 60 c.c.) until a match is obtained. Not more than 10 c.c. of standard solution should be used in making the final determination

Bismuth.—The yellow colour formed when potassium iodide is added to a solution of bismuth in dilute sulphuric acid containing a trace of sulphurous acid is still the most suitable for quantitative work. The addition of organic bases such as cinchonine (Feigl and Neuber, Z. anal. Chem. 1923, 62, 369) or quinine (Aubry, J. Pharm. Chim. 1922, 25, 15), although increasing the sensitivity, is not very reliable. The bismuth is dissolved in sulphuric acid and suitably diluted ; to about 15 c.c. of the solution to be tested are added 10 c.c. of 2% solution of potassium iodide, any free iodine which may be liberated is removed by adding 0 6% sulphurous acid, and the liquid diluted to 30 c.c. The yellow colour due to bismuth is matched against standards containing the same concentration of free sulphuric acid. The standard solution is prepared by dissolving 0 05 g. of metallic bismuth in 10 c.c. of concentrated sulphuric acid and diluting to 1 litre with water. (" Report of The Fiscal Policy Joint Committee, Brass, Copper and Nickel Silver Industries, on The Determination of Bismuth in Copper, 1935 " ; abstracted, Analyst, 1935, 60, 554).

Chromium.—In acid solution chromates form a soluble violet compound with diphenylcarbazide and the reaction can be employed for colorimetric determination. The liquid containing chromate is acidified with sulphuric or acetic acid and mixed with a small quantity of a 0 2% solution of diphenylcarbazide in a mixture of 1 part of glacial acetic acid and 9 parts of alcohol. Chromium salts in solution may be first oxidised by acidifying with a

mineral acid and adding a little bromine water followed by excess of sodium hydroxide. After mixing, the excess of bromine is removed by the addition of a trace of phenol, the reagent added and the mixture acidified with dilute sulphuric acid. Hg, Mo, Co, Cu, Pb, Ni, and Ag all interfere; permanganate, if present, may be removed by boiling with alcohol. The test is sensitive to 1 part in more than a hundred millions (Cazeneuve, Compt. rend. 1900, **131**, 346; Stover, J. Amer. Chem. Soc. 1928, **50**, 2363).

Cobalt.—This metal is conveniently determined by using *a*-nitroso-*β*-naphthol. A reagent solution is prepared by boiling 0·1 g. of the solid with 20 c.c. of water and 1 c.c. of dilute sodium hydroxide, filtering and diluting to 200 c.c. To the neutral or slightly alkaline solution to be tested are added 5 c.c. of alkaline ammonium citrate solution (500 g. of citric acid dissolved in 250 c.c. of water and 500 c.c. of ammonia sp.gr. 0·880) and 1 c.c. of the reagent and the mixture diluted with water to 100 c.c. A claret colour is formed in the presence of cobalt. The method is suitable for concentrations between 0·01 and 0·1%. Fe, Zn, and Pb do not interfere, but more than traces of Cu, Ni and Mn should be removed (Atack, J.S.C.I. 1915, **34**, 641T; Jones, Analyst, 1918, **43**, 317). According to Bellucci (Gazzetta, 1919, **49**, 294), *β*-nitroso-*a*-naphthol is about 8 times more sensitive than *a*-nitroso-*β*-naphthol.

Chiarottino (L'Ind. Chimica, 1933, **8**, 32) has proposed the use of a freshly prepared alcoholic solution containing 0·5% of benzidine and 0·25% of dimethylglyoxime, 1 c.c. of which is added to 50 c.c. of the solution under test, previously acidified with hydrochloric acid and containing 2 g. of ammonium acetate. An intense orange colour is produced by cobaltous ions, 0·01 mg. Co giving a distinct reaction. Relatively large amounts of Pb, Hg, Al, Ba, Sr, and Ca are without influence, but Sn, Cu, Cr, and more than traces of Fe interfere; Ni may be first removed with dimethylglyoxime. The test is inapplicable in the presence of sulphates.

Copper.—Dithio-oxamide (rubeanic acid), suggested as a test for copper by Rây and Rây (Quart. J. Indian Chem. Soc. 1926, **3**, 118) has been employed for colorimetric work by Allport and Skrimshire (Quart. J. Pharm. 1932, **5**, 461), who also give a process for determining traces of copper present in iron salts. To 50 c.c. of the neutral solution under test, containing not more than 0·06 mg. Cu, 1 g. each of ammonium acetate and acetic acid are added, followed by 1 c.c. of a 0·1% alcoholic solution of dithio-oxamide, and the yellow to olive-green coloration is matched by preparing standards. No commonly occurring colourless ions interfere. To determine copper in iron salts and medicinal preparations, the material (about 2 g.) is oxidised by heating with sulphuric acid and 30% hydrogen peroxide, the residue dissolved in hydrochloric acid and the solution treated with citric acid followed by a slight excess of ammonia; the copper is then extracted by shaking with a 0·1% chloroform solution of diphenylthiocarbazone, the extracts evaporated to dryness, the excess of reagent in the residue destroyed by wet-combustion and the resulting acid solution diluted, neutralised and examined for copper as above.

Sodium diethyldithiocarbamate is also frequently employed, but many other metals interfere (Delépine, Compt. rend. 1908, **146**, 981; Callan and Henderson, Analyst, 1929, **54**, 650). For the determination of traces of copper in iron salts, removal of iron by ammonia is inapplicable owing to partial adsorption of copper by ferric hydroxide (Hamence, Trans. Faraday Soc. 1934, **30**, 299). Haddock and Evers (Analyst, 1932, **57**, 495) avoid this difficulty by extracting the coloured copper compound formed when the reagent is added to alkaline ferric iron solutions containing ammonium citrate by means of carbon tetrachloride and measuring the depth of the resulting coloured extract with a Lovibond tintometer, the value of the yellow units being correlated with the amount of copper present. The method is convenient, but is inapplicable in the presence of more than 0·1 g. of iron. The same reagent is employed by Sylvester and Lampitt (Analyst, 1935, **60**, 376) for the determination of copper in foods, the preliminary isolation being effected by extraction with diphenylthiocarbazone.

Iron.—Thioglycollic acid which, in the presence of ammonia, produces a purple colour with a trace of either ferrous or ferric iron, is the most useful reagent for colorimetric determinations (Lyons, J. Amer. Chem. Soc. 1927, **49**, 1916). Citric acid is added to the neutral or slightly acid solution under test, followed by 0·2 c.c. of thioglycollic acid; on rendering slightly alkaline with ammonia, the colour due to iron develops to a maximum in about 2 minutes and is permanent for 15 minutes. The test is sensitive to 1 part of iron in 5 million parts of solution. Co, Ni, Cr and oxidising agents interfere, but otherwise the test is applicable in the presence of many of the common metals and acid radicals. Sulphites should be oxidised with potassium permanganate and excess of the latter removed with oxalic acid.

Lead.—The well-known sulphide method is still probably the best. For an account of precautions which should be observed and details for securing accurate results, *see* Reith and de Beus (Z. anal. Chem. 1935, **103**, 13; Analyst, 1935, **60**, 836). A method for the isolation of traces of lead from organic material and from all other common metals except bismuth and thallium has been worked out by Allport and Skrimshire (Analyst, 1932, **57**, 440).

Magnesium.—The "spot test" employing *p*-nitrobenzeneazoresorcinol may be modified for the colorimetric determination. It is necessary to add a protective colloid such as starch-glycerite.[1] Owing to the interference of other metals the method has only a limited application. Titan-yellow, proposed as a reagent for magnesium by Kolthoff (Chem. Weekblad, 1927, **24**, 254), is useful although the sensitive range is limited. Traces of magnesium in calcium salts may be separated without loss by

[1] A transparent jelly made by heating at 140° a mixture of 10 g. of starch, 20 c.c. of water, and 70 c.c. of glycerol. (Thrun, Ind. Eng. Chem. Anal.], 1930, 2, 8).

adsorption and subsequently determined as follows: To the boiling solution to be tested (containing about 0·4 g. Ca), occupying a volume of approximately 40 c.c. and slightly acidified with acetic acid, are added slowly 22 c.c. of 10% ammonium molybdate solution and the mixture is boiled for 15 minutes. After cooling, the volume is adjusted to 50 c.c. and the mixture filtered. An appropriate quantity of the filtrate is diluted to 20 c.c. with water, and 0·5 c.c. of a 0·1% aqueous solution of titan-yellow added, followed by 10 c.c. of 5*N*-NaOH. The standards for comparison should not contain more than 0·05 mg. Mg, since the pink colour produced does not show clear gradation with larger quantities ("'AnalaR' Standards for Laboratory Chemicals," 1937, p. 61).

Manganese.—Oxidation to permanganate by means of periodate is best for colorimetric work. The reaction is conducted in mineral acid solution by 10–15 minutes' boiling with an excess of potassium periodate and the resulting pink colour matched with appropriate standards. Any reducing substances which may be present, such as ferrous iron, should be oxidised by preliminary boiling with nitric acid. The effect of ferric salts on the final colour should be counteracted by introducing the same amount into the standards (Willard and Greathouse, J. Amer. Chem. Soc. 1917, 39, 2366).

Molybdenum.—The thiocyanate reaction first described by Braun (Z. anal. Chem. 1867, 6, 86) can be applied quantitatively. To the solution containing between 0·001 and 10·0 mg. of molybdenum are added 8 c.c. of concentrated hydrochloric acid, 5 c.c. of 2% aqueous solution of stannous chloride and 5 c.c. of 10% aqueous solution of potassium thiocyanate, and the mixture is diluted to 50 c.c. with water. The red colour produced attains its maximum intensity in 5 minutes and may be matched directly against standards, or extracted with ether. Hurd and Allen (Ind. Eng. Chem. [Anal.], 1935, 7, 396) found that with low concentrations of acid (0·5%) the colour reaches a maximum in 8 minutes and then fades, but with 5% of hydrochloric acid some fading occurs in the first few minutes, but thereafter the colour remains nearly constant; these tests were conducted in the presence of 1% of potassium thiocyanate and 0·8% of stannous chloride. A higher concentration of hydrochloric acid induces fading. Not less than 0·6% of potassium thiocyanate should be present in the final mixture, and the concentration of stannous chloride should exceed 0·1%. If sulphuric acid is employed, the final mixture should contain 10%. These investigators found that extraction of the colour with butyl acetate (James, *ibid.* 1932, 4, 89) gave anomalous results.

Nickel.—Dimethylglyoxime in association with sodium hypochlorite yields a reddish-brown colour with nickel which is permanent for several hours (Jones, Analyst, 1929, 54, 582). The solution to be tested, which should be slightly ammoniacal and contain between 0·01 and 0·1 mg. Ni, is diluted to 100 c.c. with water and mixed with 2 c.c. of an almost saturated alcoholic solution of dimethylglyoxime; 1 c.c. of sodium hypochlorite solution is then added, the resulting colour being compared with standards similarly prepared. The colour develops to its maximum intensity in a few minutes.

Silver.—The recent application of this metal as a sterilising agent has added importance to its colorimetric determination. The qualitative test using *p*-dimethylaminobenzalrhodanine (Feigl, Z. anal. Chem. 1928, 74, 380) has been applied quantitatively by Schoonover (Bur. Stand. J. Res. 1935, 15, 377). The neutral solution to be tested is mixed with 0·5 c.c. of 4*N*-HNO_3 and sufficient water to produce 15 c.c. To this mixture 0·5 c.c. of a 0·02% alcoholic solution of *p*-dimethylaminobenzalrhodanine is added, and the pink or red colour produced matched against standards prepared with silver nitrate solution. The test is applicable to solutions containing between 0·06 and 9·0 mg. of Ag per litre. Soft glass adsorbs silver and it is best to employ apparatus made of fused silica, but, provided the solutions be not warmed, Pyrex glassware may be used. Au, Pt, Pd, and univalent Cu and Hg also react, while calcium carbonate, sodium nitrate and ammonium nitrate increase the depth of the colour due to silver if any of them are present in amount greater than 1 mg. per litre. Chlorides may be removed by evaporating the test solution with nitric acid in a silica dish.

Tin.—Although a number of colour tests have been proposed, no really satisfactory quantitative method is available. A study of the cacotheline test (Newell, Ficklen and Maxfield, Ind. Eng. Chem. [Anal.], 1935, 7, 26) has shown that it is quite unsuitable for quantitative work and that, even as a qualitative test, it is subject to considerable limitations. The most promising process for colorimetric work is that proposed by Huttig (Chem.-Ztg. 1923, 47, 341) and modified by Feigl (*ibid.* p. 561). In the following description further alterations have been made by the writer, in whose hands the method has given encouraging results. A reagent is made by dissolving 1 g. of molybdenum trioxide in 15 c.c. of *N*-NaOH, diluting with 10 c.c. of water and acidifying with 3 c.c. of *N*-HCl; 70 g. of ammonium acetate are dissolved in 120 c.c. of water and added to the molybdenum solution, and the mixture diluted to 200 c.c. with more water. The neutral solution under test, containing between 0·1 and 1·0 mg. of bivalent tin, is mixed with 5 c.c. of the above reagent and 10 c.c. of 3*N*-HCl, and the liquid finally diluted with water to 50 c.c. The blue colour produced attains its maximum intensity in about 2 minutes and is permanent for some hours. The test is applicable in the presence of appreciable amounts of Zn, Cd, As, Sb, Al, Ba, Ca, and Mg and smaller quantities (large relative to the Sn) of Cu, Pb, and Fe. All these, however, tend to alter the shade of colour, and the standards should contain approximately the same quantities of substances other than tin which are present in the solution under examination. The method might be used for the determination of traces of tin occurring in zinc die castings. When the test is conducted as described above, extraction of the colour with amyl alcohol, as suggested by Feigl, is inapplicable.

Substituted 1:2-dimercaptobenzenes have been suggested for the colorimetric determination of tin by Clark (Analyst, 1936, **61**, 242), and 4-methyl-1:2-dimercaptobenzene ("dithiol") is commercially available. A few drops of a freshly prepared solution containing 0·2% of this reagent and 0·4% of thioglycollic acid in 1% aqueous solution of sodium hydroxide is added to the liquid under test which should be previously acidified with hydrochloric acid; a red precipitate is produced in presence of bivalent and quadrivalent Sn. Most other heavy metals give yellow precipitates, but those due to Cu, Ni and Co are black, while Bi forms a brick-red compound. Satisfactory quantitative results can be obtained by adding agar-agar and measuring the colour by reflected light using a Lovibond tintometer (Clark, Analyst, 1937, **62**, 661).

Titanium.—The method originally proposed by Weller (Ber. 1882, **15**, 2593) in which hydrogen peroxide is employed has not been improved upon by the newer reagents. The sodium salt of chromotropic acid, proposed as a test for titanium by Hofmann (Diss., Munich, 1902), although useful for qualitative purposes, is not so satisfactory in colorimetric work owing to the strong coloration produced by traces of iron. In applying the hydrogen peroxide method the solution to be tested, which may be derived from a potassium pyrosulphate fusion of the original sample, should contain not less than 5% of sulphuric acid. An appropriate quantity is transferred to a Nessler glass, 2 c.c. of 3% hydrogen peroxide added and the mixture diluted to 50 c.c. with 5% sulphuric acid; in the presence of titanium a yellow colour is produced. A standard solution is prepared by heating 0·3 g. of potassium titanifluoride with several successive portions of concentrated sulphuric acid in a platinum dish until all the fluorine is evolved, care being taken not to evaporate to dryness, and finally diluting to 1 litre with 5% sulphuric acid (1 c.c.=0·1 mg. TiO_2). Cr, V, Mo interfere since they also give colours with hydrogen peroxide.

Vanadium.—The intensity of the brownish-red colour produced by the action of hydrogen peroxide upon acidified vanadate solutions depends upon the relative proportions of the oxidising agent, free sulphuric acid and vanadium present. Meyer and Pawletta (Z. anal. Chem. 1926, **69**, 15) find that a considerable excess of acid is required and that the ratio $V : H_2O_2$ should *not* exceed unity. The substance to be tested is fused with sodium carbonate or nitrate, the mass dissolved in 15–20% sulphuric acid, and after some minutes the solution is treated with one drop of 3% hydrogen peroxide. Under these conditions it is stated that the test will detect 1 part of V in 160,000 parts of liquid.

Acid Radicals.

Fluorides.—The colorimetric method depending upon the bleaching action of fluoride ions on acidified pertitanate solutions was originally proposed by Steiger (J. Amer. Chem. Soc. 1908, **30**, 289) and developed by Merwin (Amer. J. Sci. 1909, **28**, 119). To about 50 c.c. of the approximately neutral solution under test are added 10 c.c. of 65% sulphuric acid, 3 c.c. of 3% hydrogen peroxide and 10 c.c. of standard titanium sulphate solution. The mixture is diluted to 100 c.c. and the tint compared with that of mixtures made with known amounts of fluorine prepared from standard sodium fluoride solution. The titanium sulphate solution is prepared in the same way as indicated in the description of the colorimetric determination of titanium, excepting that it should be ten times stronger (1 c.c.=1·0 mg. TiO_2). For the determination of fluoride in basic slag by this method *see* Warren, Gimingham, and Page (J. Agric Sci. 1925, **15**, 516) whose method is given by Mitchell and Ward ("Modern Methods in Quantitative Chemical Analysis," Longmans, Green & Co., 1932).

Nitrates.—Kolthoff and Noponen (J. Amer. Chem. Soc. 1933, **55**, 1448) recommend a 0·006*M* solution of sodium diphenylamine-sulphonate as a convenient reagent. To 10 c.c. of the cold solution to be tested, containing 1% of potassium chloride, are added 10 c.c. of concentrated sulphuric acid, the mixture being kept cool under running water, and 0·1 c.c. of the reagent. Standards are prepared with 1% potassium chloride solution containing from 0·1 to 5·0 mg. of nitrate per litre. The interference of nitrites can be eliminated by boiling with ammonium chloride; urea should not be used since it disturbs the formation of the colour due to nitrate. Blom and Treschow (Z. Pflanz. Düng. 1929, **13**, A, 159) employ 2:4-xylenol as a reagent for the colorimetric determination of nitrates occurring in soils and plants. The 5-nitro-2:4-xylenol formed by the reaction is volatile in steam and gives an intense coloration with sodium hydroxide. McVey (J. Assoc. Off. Agric. Chem. 1935, **18**, 459) has applied the method to meat products. 5–10 g. of the minced sample are extracted by heating with 80 c.c. of water for an hour, the mixture cooled, diluted to 100 c.c., filtered, and 40 c.c. of the filtrate rendered just acid by means of sulphuric acid to bromocresol-green indicator. Nitrites are oxidised by adding 0·2*N*-potassium permanganate drop by drop until a faint pink colour persists for 1 minute; the proteins are then precipitated by adding 1 c.c. of 10% sulphuric acid, followed by 1 c.c. of 20% solution of phosphotungstic acid. The mixture is diluted to 50 c.c., and an aliquot part of the filtrate, containing 0·15–0·25 mg. of nitrate and not exceeding 20 c.c. in volume, is treated with silver ammonium hydroxide solution (*see below*) to precipitate any chlorides and to remove excess of phosphotungstic acid. Three volumes of 85% sulphuric acid are now added, the liquid cooled to 35°, and treated with three drops of a 1% aqueous solution of 2:4-xylenol; the product is maintained at 35° for 30 minutes, then diluted with 100 c.c. of water, and 50 c.c. of the liquid are distilled into a receiver containing 5 c.c. of 1% sodium hydroxide; the liquid, which will be coloured yellow or orange-red if nitrates are present in the sample, is diluted to an appropriate volume. A standard distillate is prepared by mixing 1 c.c. of 0·0375*N*-nitric acid (1 c.c.=0·5 mg. nitrate nitrogen) with 4 c.c. of water and 15 c.c. of 85% sulphuric acid, cooling to 35°, and carrying out the nitration

and distillation as described above. After dilution to 500 c c., suitable quantities are employed to make a series of standards in Nessler glasses. The silver ammonium hydroxide solution is made by dissolving 5 g. of silver sulphate in 60 c.c. of 10% ammonia, boiling until the volume is reduced to 30 c.c. and then diluting with water to 100 c.c.

Phosphates.—Denigès's modification of the coeruleomolybdic-stannous chloride test (Compt. rend. 1920, **171**, 802) has been improved by Truog and Meyer (Ind Eng. Chem. [Anal.], 1929, **1**, 136). To the neutral solution under test are added 4 c c. of a 2 5% solution of ammonium molybdate in 10N-sulphuric acid and 0 3 c.c. of freshly prepared stannous chloride solution (*2·5% $SnCl_2,2H_2O$ in 10% concentrated hydrochloric acid*) and the mixture diluted to 100 c c. The blue colour produced should be matched within 10 minutes. The standard solution (1 c.c.=0 005 mg. P) is made by dissolving the appropriate amount of potassium dihydrogen phosphate in 0 001N-sulphuric acid. The test is sensitive to 0 005 mg. P. Up to 700 p p m. of SiO_2 may be present without influencing the results, but more than 6 p.p.m. of ferric iron or 20 p p.m. of TiO_2 interfere, while 200 p p m. of potassium nitrate reduce the colour intensities by about 10% Appreciable quantities of Al, Mn, Ca and Mg do not affect the results Arsenates behave similarly to phosphates but may be first reduced by treatment with hydrogen sulphide in acid solution and the test for phosphates subsequently applied after the liquid has been well boiled and sulphur removed by filtration with paper pulp Of the tests using organic reducing agents that proposed by Tschopp and Tschopp (Helv. Chim Acta, 1932, **15**, 793) is the most reliable. To 25 c.c. of the solution under test are added 1 c c. of ammonium molybdate solution (5% in N-H_2SO_4) and 2 c c. of a solution containing 0 1% of p-methylaminophenol sulphate (metol), 20% of sodium metabisulphite and 0 5% of sodium sulphite (crystal). The mixture is warmed to 60° for 10 minutes, cooled, diluted to 50 c c. and the blue colour matched with standards similarly prepared. The test will detect 0 004 mg. P ; it responds to silicates, but under the above conditions it is seventeen times less sensitive to silicates than to phosphates.

Silicates.—The colorimetric method depending upon the production of a yellow colour on the addition of an acid solution of ammonium molybdate introduced by Schreiner (J. Amer. Chem. Soc. 1903, **25**, 1056) was modified by Isaacs (Bull. Soc. Chim. biol. 1924, **6**, 157), who employed sodium sulphite in order to form the blue complex. Several alternative reducing agents have been recommended by subsequent investigators. Phosphates also react but Parri and Scotti (J. Pharm. Chim. 1933, [viii], **18**, 513) prevent their interference by adding ammonium citrate and Rodillon (Bull. Biol. Pharm. 1934, **1**, 33) has further modified the method with the object of depressing the sensitivity to phosphates. The solution to be tested is acidified with dilute sulphuric acid, and 1 c.c. mixed with 1 c.c. of a 10% solution of ammonium molybdate, 1 c.c. of 95% alcohol and 1 c c. of ammonium citrate solution (2 g. of citric acid in 10 c.c. of water and 10 c.c. of strong ammonia) and the mixture heated to 60° until the yellow colour is fully developed. After cooling 0·35 g. of hydroxylamine hydrochloride and 0 35 g. of sodium hyposulphite are dissolved in the mixture, which is then diluted to 10 c c., or other convenient volume, filtered if necessary, and the blue colour matched against standards similarly prepared. The standard silicate solution is conveniently made by fusing 0 05 g of pure silica with 2 g. of sodium bicarbonate and diluting the solution of the fused mass to 500 c c.

Sulphates.—Hubbard's method (J. Biol. Chem. 1927, **74**, V ; 1930, **88**, 663) has been modified by Cuthbertson and Tompsett (Biochem. J. 1931, **25**, 1237). It is applied to the determination of sulphates in blood, but the process should be suitable for general application where minute quantities have to be determined. To 2 5 c.c. of the liquid to be tested, contained in a 15 c.c. centrifuge tube, are added 5 c.c. of a 0 5% solution of benzidine in acetone. After mixing, standing for 30 minutes, and centrifuging, the supernatant liquid is poured off, the precipitate of benzidine sulphate washed twice with acetone, and the tube inverted over filter paper until the interior has dried The precipitate is then dissolved by warming with 1 c.c. of N-HCl and, after cooling, 0 5 c c. of a 0 1% aqueous solution of sodium nitrite is added, followed after the lapse of 1 minute, by 2 5 c c of a 15% aqueous solution of sodium hydroxide and then 2 5 c.c. of a 1% solution of thymol in 10% aqueous sodium hydroxide. The red colour produced is compared with standards made by mixing 2 c c. of standard benzidine hydrochloride solution with 1 c.c. of sodium nitrite solution and, after standing 1 minute, adding 5 c.c. of 15% sodium hydroxide, shaking and mixing with 5 c c. of the alkaline thymol solution. The standard benzidine hydrochloride solution is prepared by diluting a 0 4014% solution of the hydrochloride in N-HCl (1 c.c. of which is equivalent to 0 5 mg. of sulphur) so that a series of standards is obtained in which 1 c c. contains benzidine equivalent to 0 0025 up to 0 08 mg. of sulphur.

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GAS ANALYSIS.

The Methods of Gas Analysis.—Methods of gas analysis may conveniently be grouped under the following heads : (i) *Volumetric Methods*—(This term is here restricted to processes in which gas volumes are measured.) The principle, which was worked out by Cavendish and by Bunsen ("Gasometrische Methoden," 2nd ed. 1887) is to measure the volume (*i.e.* molar quantity) of a gas sample, and by means of selective chemical reactions remove the various constituents in succession, the quantities so removed being measured by

the resulting diminutions in volume. (ii) *Special Chemical Methods.*—These comprise colorimetric, titrimetric, and gravimetric methods, and are generally used where volumetric methods are inapplicable, owing to the nature of the gases present, or to the small proportion of the constituent tested for. (iii) *Physical Methods.*—In these, constituent gases are determined by virtue of their physical properties.

Sampling.—The two important considerations in taking a gas sample are (i) the taking of a representative sample, and (ii) subsequent protection of the sample from change in composition. In sampling gases from large bottles, autoclaves, etc., care must be taken to ensure that adequate mixing of the constituents has taken place. With cylinders, especially those containing a liquid phase, the composition of the gases taken from a full and from a partly empty cylinder are not necessarily the same. Gases flowing through large pipes may differ in composition between the sides and middle of the pipe ; in such cases the sampling tube is made to pass through the pipe from one side to the other, and is pierced with holes (of appropriate different sizes) at different points, in such a way as to give a representative sample. For flue gases, the open end of the sampling tube should be exposed to the main current of ascending gases ; the exact place for the sampling tube is chosen by trial from results of tests carried out to show which position gives the best indication of fluctuating firing conditions. For taking representative samples of gases of fluctuating composition, devices have been described by Gray (J.S.C.I. 1913, 32, 1093) and by Pexton and Hutchison (*ibid.* 1929, 48, 242). Where gas of fluctuating composition is being generated at a fluctuating rate, devices are used to take the sample at a rate proportional to the rate of production (*see* " Fuel Research Board, Report for Year ended 31/3/1929 ").

A convenient vessel for taking samples of up to 100 ml. is illustrated in Fig. 1. Admission of air during sampling is prevented by blowing or drawing gas through the side-branch to remove air from the connections. Samples for precise analysis should be stored over mercury ; if stored in vessels of the type shown in Fig. 1, the gas should be at slightly positive pressure, and the capillaries leading to the taps filled with mercury. The most satisfactory way of storing small samples (up to 50 ml.) is in inverted test-tubes standing in a mercury trough. This involves, however, the use of a vessel with a siphon tube, and a suitable mercury trough, for transferring the sample to the analysis apparatus.

Rubber connections should be as short as possible, particularly where either hydrogen or carbon dioxide is an important constituent of the gas. For the sampling of hot gases, tubes of porcelain, or, where there is no danger of corrosion, iron, may be used.

Volumetric Analysis.

Apparatus for volumetric gas analysis consists essentially of (i) a device for measuring gas volumes, and (ii) devices for submitting the gas to the action of absorbents or other chemical agents. The type to be chosen out of the large number of such instruments which have been designed for various purposes depends on the approximate composition of the gases intended to be analysed, and on the accuracy required.

Measurement.—The measurement of molar quantities of gas involves measurement of volume, pressure, and temperature. In practice, it is carried out according to one of two general methods : (i) measurement of volume in a graduated vessel, at a constant pressure (usually atmospheric), or (ii) confining the gas in a constant volume and measuring its pressure by means of a mercury manometer. The gas must be kept either free from water vapour or else saturated with it ; the latter practice is almost universal (except in micro-analysis, p. 680). Temperature is kept as constant as possible ; changes of temperature during an analysis affect the apparent molar quantity according to the relation $PV=RT$, and, in addition, according to the change of vapour pressure of water with change of temperature. With many types of

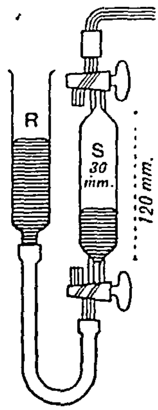

Fig. 1.

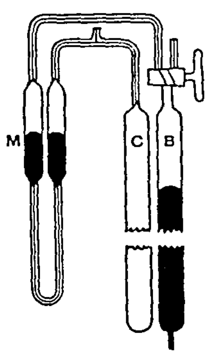

Fig. 2.

constant-pressure apparatus, the effect of variations in temperature (and also barometric pressure) is eliminated by the introduction of a " compensator ", one type of which is shown diagrammatically in Fig. 2. In this apparatus, the pressure of the gas in the measuring tube B is, by means of the differential manometer M, brought to the same pressure as that of a fixed quantity of air in the tube C ; since the effect of temperature on the gas and moisture contained in this constant volume is the same as that in M, variations in temperature are thus compensated automatically. For special analyses, involving volume measurements accurate to 0·01%, the differential manometer shown may be replaced by a tilted water manometer sensitive to 0·02 mm. of mercury, which allows volumes to be adjusted to the equivalent of 0·003% on the total volume.

As regards the treatment of the gases with the chemical reagents, some instruments are fitted with an absorption chamber which is successively filled with the appropriate reagents, while others are fitted with vessels kept permanently filled with each of the reagents, the gas being introduced into them in succession. A few of the

more important instruments are briefly described below.

Orsat Apparatus.—This is a convenient and widely used portable instrument for analyses of approximate accuracy (0 5%) and is illustrated in a simple form in Fig. 3. The gas is confined over an aqueous liquid (*e g.* 22% **NaCl**, concentrated **$CaCl_2$**, 50% glycerin) and is measured in a graduated burette of 50–100 ml. volume. The gas is brought to atmospheric pressure by levelling with the reservoir shown at the bottom of the apparatus. For absorption, the gas is transferred to any one of a number of absorption pipettes, which are all connected, through a manifold of capillary tubing, to the measuring burette ; the usual absorbents are alkali (for **CO_2**), pyrogallol (for **O_2**) and cuprous chloride (for **CO**). In Lunge's form of the Orsat apparatus, combustion of hydrogen, etc, is effected by passing the gas through a heated

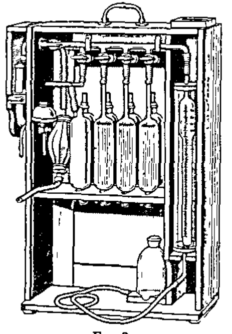

Fig. 3.

capillary tube containing palladised asbestos (p. 680) This tube, which is heated externally by means of a small spirit-lamp, is placed between the manifold and a pipette filled with the confining solution. In other designs, combustion is effected by explosion, or by means of a heated platinum wire (Sodeau, Chem. News, 1904, 89, 61). In the Hays apparatus, the glass taps are replaced by needle-valves. The Orsat type of apparatus has the advantages of portability and simplicity of manipulation, but can be used, at least in its compact and simple form, for only a small number of constituents. In the U.S.A., instruments of the Orsat type have been developed into high-precision instruments, which have mercury as confining liquid and are not at all portable. For details of such instruments, *see* Burrell and Oberfell, J. Ind. Eng. Chem. 1916, 8, 228, and Shepherd, Bur. Stand. J. Res. 1931, 6, 121 ; and for fuller details of the Orsat apparatus in its simpler forms, *see* Lunge and Ambler, "Technical Gas Analysis," London, 1934, p. 51 *et seq.*

Bone-Wheeler Apparatus—This apparatus and its modifications is probably the most widely used instrument for exact analysis in Great Britain. It is illustrated in a simple form in Fig 4. Gas is measured at constant volume in the limb *A* of the water-jacketed **U**-tube, the pressure being measured by the height of the column of mercury in the limb *B*, which is graduated in millimetres. The limb *A* has a series of graduations coinciding in level with each integral 100 mm. mark on *B*. The heights of *A* and *B* are such, that when a measurement

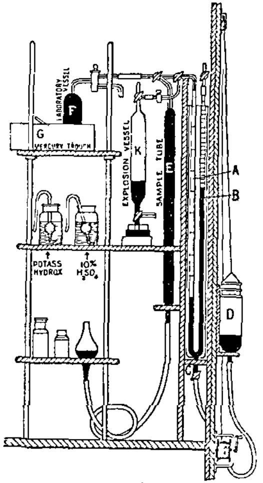

Fig. 4.

is being made, the closed space above the mercury in *B* is a Torricellian vacuum except for water vapour, both limbs being kept saturated with water by means of a small quantity of dilute sulphuric acid (2–5%). Absorption is carried out in the vessel *F*, which stands in a mercury trough ; the capillary three-way tap at the top connects to the measuring vessel and to a bottle or other vessel connected to a filter pump or other exhausting apparatus, by means of which the reagent, introduced into *F* by means of a pipette, may be removed after absorption has taken place. Combustible gases are determined by explosion with air in the vessel *K*, which is fitted with a spark-gap. In a number

of modifications (*e.g.* King, Fuel in Science and Practice, 1922, **1**, 103 ; Donnelly, Foott and Reilly, Sci. Proc. Roy. Dublin Soc. 1929, **19**, 165 ; Smith, Gas World, 1919, **71**, 342), a copper oxide tube (p. 680) is fitted. The Bone-Newitt apparatus is a modification in which the movement of the mercury is controlled from the water supply by means of a special three-way water tap. For details, *see* Himus, "Fuel Testing" (1924), pp. 185–190.

Haldane Apparatus.—This is a specialised apparatus for the determination of carbon dioxide, oxygen and relatively small quantities of combustible gases. The gas is measured at constant volume in a pipette the graduations of which usually cover 20% of the total volume ; a compensator is an integral part of the instrument. Carbon dioxide and oxygen are absorbed by alkali solution and alkaline pyrogallol respectively, kept in special vessels connected to the measuring vessel ; combustions are carried out in a separate vessel fitted with a platinum wire which can be electrically heated (p. 679). The accuracy attainable is of the order of 0·01%. The main application of the Haldane apparatus is air-analysis. It is also made in a portable form.

Ambler Apparatus.—The laboratory apparatus is a constant-volume apparatus ; the measuring vessel consists of three bulbs giving capacities of 1, 5, and 10 ml. ; pressures are measured on an external mercury manometer connected to the measuring vessel by rubber tubing. The measuring vessel is connected by a fused glass joint to a bulb (fitted with spark-gap) which serves both for absorptions and for explosion. A portable apparatus is illustrated in Fig. 5. Gas is measured in the graduated burette either at constant pressure or at constant volume, the pressure being measured by a manometer standing at the side of the measuring burette. The manometer can also be used to correct readings obtained at approximately constant pressure (by rough levelling of the mercury reservoir with the mercury in the burette) to conditions of precisely constant pressure. Absorption and combustion are carried out in a vessel which is connected to the measuring burette through a three-way tap ; the gas does not come in contact with any rubber connections during the analysis. Combustion is effected by means of electrically-heated platinum wire. The accuracy attainable is 0·1% on the total gas.

Determination of Constituent Gases.

With all these types of apparatus, the methods of determination of the constituent gases are similar. The main sources of error in determination by absorption are (i) incomplete absorption due to insufficient time of contact, the use of exhausted solution, or a chemical equilibrium being set up between the gas and the compound formed by its action on the absorbent ; (ii) physical solution of constituent gases in reagents designed for the absorption of other constituents ; this is reduced to a minimum by the use of as small quantities of reagent as possible and by saturating the reagents with the gases with which they have to come in contact. This is particularly necessary with such instruments as those of Orsat and Haldane where small volumes of reagent are not practicable. Constituents are usually determined in the following order by the methods detailed below.

Carbon Dioxide.—Absorption in alkali solution. Potassium or sodium hydroxide of 25% strength is to be recommended except for apparatus of the Orsat type where the use of 40–50% potassium hydroxide reduces the number of times necessary to refill the pipettes. Whenever high concentrations of carbon dioxide are present, appreciable error may be introduced by solution of it in rubber connections or tap grease (Branham, J. Res. Nat. Bur. Stand. 1934, **12**, 353).

Unsaturated Hydrocarbons.—These are usually absorbed after removal of carbon dioxide ; where benzene and its homologues are present, however, it is advisable to absorb these first of all (with a small quantity of concentrated sulphuric acid) as they are appreciably

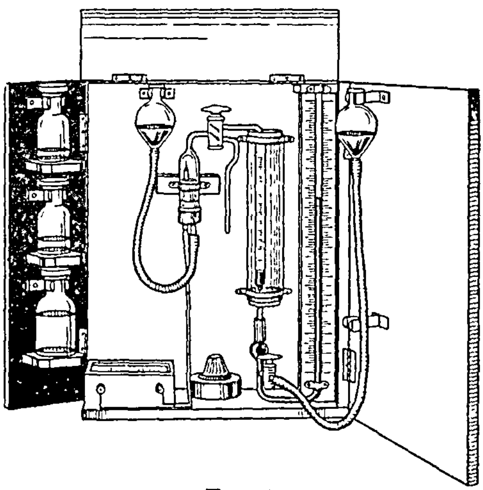

Fig. 5.

soluble in alkali solution. The most satisfactory absorbent for unsaturated hydrocarbons is fuming sulphuric acid (20–25% oleum). Absorption is usually complete in 2–5 minutes ; shaking does not greatly promote absorption, but increase of the surface of the reagent by means of glass rods, etc., accelerates the process. The temperature must be kept above 15°C. to prevent pyrosulphuric acid crystallising out. The gas must be treated with alkali solution subsequently, to absorb acid vapours.

Bromine water (10%) or bromine dissolved in 10% potassium bromide is also used for the complete absorption of unsaturated hydrocarbons.

Acetylene is absorbed by potassium mercuric iodide, made by dissolving 25 g. HgI_2 and 30 g. KI in 100 ml. water, and mixing with alkali solution immediately before use ; carbon monoxide is not affected.

Benzene may be absorbed by ammoniacal nickel cyanide (for preparation, *see* Dennis and McCarthy, J. Amer. Chem. Soc. 1908, **30**, 233).

All olefines except ethylene are removed by absorbtion by concentrated sulphuric acid ; these can be determined in the presence of ethylene treating the gas with successive small quantities (2 ml) of 87% sulphuric acid ; after four such treatments (5 minutes each) the higher olefines are absorbed, and the rate of absorption of ethylene enables a correction to be made for the absorption of it in the earlier stages (*see* Manning, *et al.*, Analyst, 1928, **53**, 224 ; Sakmin, Z. anal. Chem. 1934, **98**, 409 ; Sakmin and Michnowska, *ibid.* 1935, **100**, 264). Various metallic salts greatly accelerate the absorption of ethylene by concentrated sulphuric acid (Lunge and Ambler, *op. cit.*, p. 94)

Olefines and acetylenes can also be determined volumetrically by catalytic hydrogenation with hydrogen gas in the presence of a nickel catalyst at *ca.* 180°C (McMillan, Cole and Ritchie, Ind. Eng Chem [Anal], 1936, **8**, 105) Diolefines can be hydrogenated in the cold (Dolgoplosk, Amer. Chem. Abstr. 1936, **30**, 410) Butadiene is absorbed quantitatively by molten maleic anhydride at 100°C (Tropsch and Mattox, Ind. Eng. Chem. [Anal], 1934, **6**, 104).

Oxygen.—The usual absorbent is alkaline pyrogallol. For Orsat and Haldane pipettes, 15 g. pyrogallol in 100 ml. 50% KOH is satisfactory. For the Bone-Wheeler and similar apparatus, 25% aqueous pyrogallol and 40% alkali ($NaOH$ or KOH) are mixed in the ratio 1:4 in the absorption pipette. At 20°C. about 3 minutes' shaking effects complete absorption , below 15° absorption is inconveniently slow, the temperature effect being greater with potassium than with sodium pyrogallate. With gases containing more than about 25% of oxygen, some carbon monoxide is always evolved, giving low results. With the solution recommended for the Haldane apparatus this effect is negligible in the case of air if the solution is kept for three days before use, or alternatively heated at 100°C. for an hour (Haldane and Makgill, Analyst, 1933, **58**, 378). For use at lower temperatures and with gases containing much oxygen, a solution of 6 6 g. $NaOH$, 16 g. sodium hyposulphite and 2 g sodium anthraquinone β sulphonate in 100 ml. water is satisfactory (Fieser, J. Amer. Chem. Soc. 1924, **46**, 2639). The solution does not retain its activity after more than about a week's storage (*see also* Quiggle, Ind. Eng Chem. [Anal], 1936, **8**, 363).

Solid phosphorus confined over water is widely used in Orsat pipettes ; it may also be confined over mercury if the sticks are kept moist with water. The oxygen content should not exceed 50% and the temperature must be above 15°C. Absorption is complete in about 3 minutes Quantities of oxygen up to 0 2% may remain unabsorbed however long the contact with the phosphorus (Ambler, Analyst, 1934, **59**, 593). Hydrogen and carbon monoxide may be slightly attacked, the contractions arising (in the case of hydrogen) giving high oxygen figures (*l c.*).

Ammoniacal Copper.—This is the most efficient absorbent for oxygen, provided carbon monoxide, acetylene and ethylene, which it also absorbs, are absent. A roll of copper gauze is immersed in a mixture of equal volumes of ammonia (sp gr. 0 96) and saturated ammonium chloride or carbonate. Absorption takes place rapidly on the surface of the copper, and shaking is unnecessary. The reagent is efficient at temperatures as low as −7°C.

Carbon Monoxide.—The usual reagent is ammoniacal cuprous chloride. A satisfactory composition recommended by Moser and Hanika (Z. anal. Chem. 1926, **67**, 448) contains 11–12% $CuCl$ and 13–14% NH_3, the remainder being water. The solution is made up directly from solid cuprous chloride, water and aqueous ammonia. Absorption is usually effected by 1 minute's shaking ; it is not, however, complete, solutions which have already absorbed more than 0 05 vol CO per unit volume leaving appreciable amounts unabsorbed (Ambler, Analyst, 1926, **51**, 266) For this reason it is necessary to use at least two successive lots of reagent, the last consisting of practically unused solution. With the Orsat apparatus, it is advisable to keep two pipettes filled with reagent ; with apparatus of the single absorption-vessel type, two, or preferably, three successive small lots of unused reagent are used. The gas must be subsequently washed with water to remove ammonia Acid, and neutral saline solutions of cuprous chloride are also used (Moser and Hanika, *l c.* ; Bruckner and Gröbner, Gas u Wasserfach, 1935, **78**, 269), but are not satisfactory for precise work. Ammoniacal cuprous lactate (Gump and Ernst, Ind. Eng Chem. 1930, **22**, 382) is used in a similar way. Iodine pentoxide suspended in fuming sulphuric acid (22% I_2O_5 in "10% oleum") oxidises carbon monoxide rapidly , the carbon dioxide produced is subsequently absorbed with alkali. For details of the reagent and its application, see Lunge and Ambler, *op. cit* , p. 107.

Combustion methods for CO are dealt with below. For a volumetric method based on the reaction $3H_2+CO=CH_4+H_2O$ under the influence of nickel catalyst, *see* Lunge and Ambler, *op cit* , p. 226 ; Schuftan, Z. angew. Chem. 1926, **39**, 276 ; Pieters, Z. anal. Chem. 1931, **85**, 50.

Hydrogen.—Although various absorbents for hydrogen have been described (*op. cit.* pp 109–114), it is usually determined by oxidising it to water, either with oxygen or by some oxidising agent. In a general gas analysis, the determination of hydrogen (together with that of methane) is usually carried out after the removal of carbon monoxide as above ; in some cases, however, carbon monoxide is determined by combustion together with the hydrogen. Where a carbonaceous gas is oxidised together with the hydrogen, its amount is determined by subsequently determining the carbon dioxide produced. Measurement of the amount of oxygen consumed in the combustion (by subsequent absorption by pyrogallol) provides a further check. The use of these three data (contraction, CO_2, and O_2 consumed) permits the determination of three different constituents by one combustion, by means of the characteristic values of the above three quantities in the following table :

TABLE I.—VOLUME EFFECTS ON COMBUSTION OF GASES WITH OXYGEN.

	Vol. effect per vol. combustible gas.		
	(a) Contraction	(b) CO_2	(c) O_2 Consumed
H_2	$1\frac{1}{2}$	0	$\frac{1}{2}$
CO	$\frac{1}{2}$	1	$\frac{1}{2}$
CH_4	2	1	2
C_2H_6	$2\frac{1}{2}$	2	$3\frac{1}{2}$
C_nH_m (*i.e.* any hydrocarbon) .	$\frac{m}{4}+1$	n	$n+\frac{m}{4}$

Methods of Effecting Combustion.—Explosion.—After removal of such gases as are determined

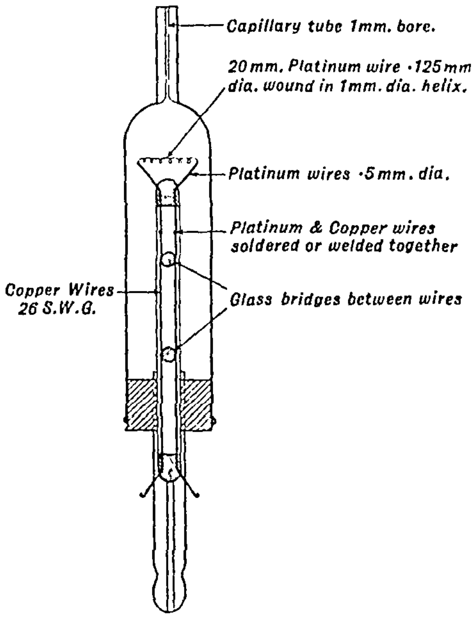

FIG. 6.

by absorption, excess of air or oxygen is added to the residue, and the gas transferred to the explosion vessel, which is usually fitted with a platinum wire spark-gap ; the spark is produced by a coil, or, more conveniently, a magneto. The chief source of error or failure in explosion analysis is an incorrect proportion of the combustible gas in the explosive mixture. If the proportion is too low, explosion does not take place, or is incomplete ; if it is too high, oxides of nitrogen are produced, giving excessive contractions and fictitious carbon dioxide. In the case of hydrogen, the hydrogen content must be between 10 and 20% (Ambler, Analyst, 1930, 55, 436) ; for methane the corresponding limits are approximately 6·0 and 8·3%, and for mixtures containing both these gases, proportionately intermediate figures. The explosion method appears to be unreliable where considerable proportions of higher paraffins are present (Misteli, J. Gasbeleucht. 1905, 48, 802). In the writer's experience the determination of carbon monoxide by explosion is unsatisfactory.

Catalytic Combustion with Platinum.—In contact with platinum wire at *ca.* 950°C., all combustible gases are oxidised in the presence of oxygen. The usual method of carrying out the process is by means of a platinum wire electrically heated. Hydrogen and carbon monoxide are oxidised at much lower temperatures. Fig. 6 illustrates a simple type of slow combustion pipette, in which the leads to the platinum wire (0·125 mm. diam.) are fused through a single glass tube (Harden, J. Sci. Instr. 1931, 8, 332). Fig. 7 represents a "bubbling pipette" (Ambler, *ibid.* 1931, 8, 18), in which a gas containing large proportions of combustibles, such as would explode if directly mixed with oxygen and exposed to the hot wire, can be burned in a controlled slow

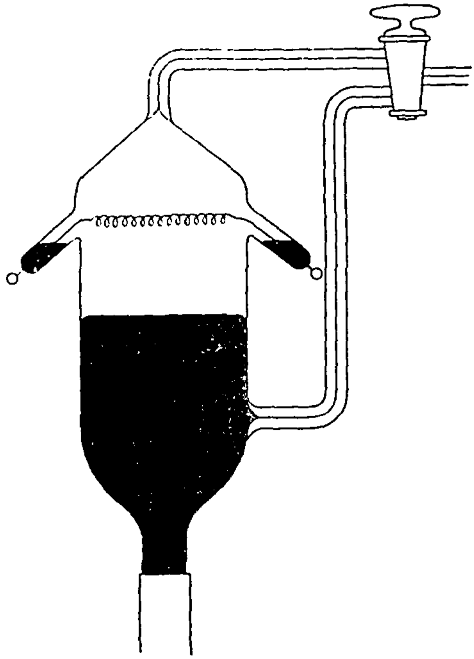

FIG. 7.

stream of oxygen which is bubbled through the side limb (*see also* Bayley, Canad. J. Res. 1932, 7, 680). Fig. 8 shows a Levy silica-platinum capillary (J.S.C.I. 1912, 31, 1153) ; the combustible gas, with the requisite excess of air or oxygen added, is passed backwards and forwards through the capillary. Where the proportion of the less combustible gases (hydrocarbons) is high, it is desirable to increase the surface of platinum by using foil ; this is contained in a silica tube heated externally and previously evacuated, the residual gas being removed by evacuation (for details, *see* Hyde and Mills, "Gas Calorimetry," p. 328). One of the most useful applications of catalytic combustion by platinum is the *fractional combustion* of hydrogen and carbon monoxide ; with platinum wire at dull red-heat, these gases are completely burned whereas methane is not

affected at all; 1 minute's treatment in the platinum wire pipette is sufficient (Whitaker, Fuel in Science and Practice, 1925, 4, 250). The combined percentage of hydrogen and CO must not exceed 3 (with samples of 20 ml.), or the heat of combustion raises the temperature of the wire and some methane is also burnt (with samples of 2–3 ml. as much as 8% of these may safely be present). If these gases are present in proportions above the lower explosion limit, explosion will take place however low the initial temperature of the platinum. With the bubbling pipette, the slower rate of combustion of CO makes it advisable, if it is present in large proportions, to remove it previously; hydrogen can then be conveniently burned in a stream of air with the wire at dull red-heat. Higher paraffins are probably slightly oxidised with the wire at dull red-heat, but data on this point are sparse; fractional combustion cannot be carried out in the presence of unsaturated hydrocarbons Platinised silica-gel at 300°C. has also been used for the fractional combustion of hydrogen and CO (Kobe and Arveson, Ind. Eng. Chem. [Anal.] 1933, 5. 110; Kobe and Brookbank, *ibid.* 1934, 6, 35). Palladium may be used in a very similar way to platinum; the combustion of methane is more rapid than with platinum. A number of fractional combustion processes using palladium have been described, but the discrepancies indicate that personal factors are appreciable. Palladised asbestos is used in the Lunge-Orsat apparatus for the fractional combustion of hydrogen (not CO) in the presence of methane (for details, *see* Lunge and Ambler, *op. cit.*,

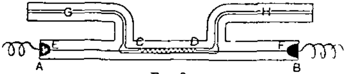

FIG. 8.

p. 135). Hauser (Bull. Soc. chim. 1923, 33, 1199) has extended the use of palladised asbestos to the combustion of carbon monoxide, by the addition of rhodium black.

Combustion with Copper Oxide.—Copper oxide at 270°–295°C. oxidises hydrogen and carbon monoxide rapidly and completely, methane being unaffected. The oxygen is supplied by the copper oxide; if oxygen is present, however, the oxide acts as a catalyst and is not reduced. The volume changes on combustion with copper oxide, in the absence of oxygen are shown in the following table:

TABLE II.—VOLUME EFFECTS ON COMBUSTION OF GASES WITH COPPER OXIDE.

	Vol effects per vol combustible gas	
	(a) Change of volume on combustion	(b) CO_2 produced
H_2 . .	-1	0
CO. . .	0	1
CH_4 . .	0	1
C_2H_6 .	$+1$	2
C_nH_m . (any hydrocarbon)	$+n-1$	n

The fractional combustion of hydrogen and CO cannot be carried out in the presence of unsaturated hydrocarbons (these are completely oxidised at 700°); if the proportion of higher paraffins is above about 5% these are slightly attacked, and accordingly (King and Edgcombe) advise the absorption of CO first and the combustion of the hydrogen at 230°–250°; *see* Lunge and Ambler, *op cit*, p. 144). Methane and its homologues may be determined subsequently by combustion with copper oxide at 950°–1,000°; some oxygen is produced by dissociation and should be eliminated by cooling the furnace to lower temperatures at which it is reabsorbed (Bunte and Wunsch, Gas- u. Wasserfach, 1923, 66, 481). Combustion with oxygen, according to one or other of the methods previously mentioned is, however, preferable.

Micro Gas Analysis

For the general analysis of gas samples of 0 01–0 1 ml, the same principles are employed as with larger samples, but with a radically different technique. The basis of this technique, worked out by Reeve (J.C.S. 1924, 125, 1946) and developed by a number of other workers (Christiansen, J. Amer. Chem. Soc. 1925, 47, 109; Christiansen and Huffmann, Z. anal. Chem. 1930, 80, 435; Blacet and Leighton, Ind. Eng. Chem. [Anal.], 1931, 3, 226; Blacet, MacDonald and Leighton, *ibid.* 1933, 5, 272; Swearingen, Gerbes and Ellis, *ibid.* 1933, 5, 369, Andreev and Neuman, J. Appl. Chem. Russia, 1935, 8, 1100; Seevers and Stormont, Ind. Eng. Chem. [Anal], 1937, 9, 39; Blacet and Volman, *ibid* 1937, 9, 44), is to measure the gas, dry, in a calibrated capillary tube of *c.* 0 5 mm. bore, and to absorb by means of small quantities of solid reagents introduced on the end of a platinum wire into the gas which is transferred for the purpose into a tube of *c.* 5 mm. bore. The best diameter for the capillary tube is about 0 7 mm.; it is more convenient for it to be horizontal than vertical. In most of the processes which have been described, the gas is transferred for absorption to a small inverted test-tube standing in a mercury-trough, the measuring tube terminating in a thin siphon tube, with its end ground to fit the inner surface of the top of the test-tube. In an apparatus designed by Ambler and Sutton, the form of appliance incorporates some new and useful features which have found to be of service The horizontal measuring tube

terminates in a wider vertical tube with its open lower end dipping into a mercury trough. Whichever principle is used, the absorbent is introduced into the gas in the form of a bead fused on the end of a platinum wire (c. 0·5 mm. diam.). Where solid reagents are not available, a porous bead made of sintered glass or of a mixture of kaolin and powdered porcelain may be impregnated with a liquid absorbent. The various gases are determined as follows:

Carbon Dioxide.—A bead of solid caustic alkali is made by touching a small piece of solid alkali with the heated platinum wire, and fusing it into a regular form in an electrically heated spiral; the bead should be moist enough to show a shining surface, otherwise absorption is slow.

Water Vapour.—This is removed at the beginning of an analysis and after any other process (*e.g.* combustion of hydrogen) in which it may be produced. The absorbent is a bead of phosphorus pentoxide, made in the same way as the alkali bead.

Oxygen.—A bead of yellow phosphorus, washed with water and then with alcohol, dried rapidly in a stream of nitrogen, and immediately placed under the surface of mercury, gives very rapid absorption. With air this usually inflames; phosphorus not treated in this manner is inconveniently slow. If combustible gases are present, a porous bead impregnated with alkaline pyrogallol is advisable; the reagent is contained in an inverted test-tube standing in the mercury trough of the apparatus.

Unsaturated Hydrocarbons.—Porous bead impregnated with sulphuric acid or oleum.

Ammonia.—Fused potassium hydrogen sulphate.

Carbon Monoxide.—Ammoniacal cuprous chloride in a porous bead, or precipitated silver oxide, pressed while moist, dried, and a suitable piece attached to the wire by means of waterglass. The latter reaction is

$$2Ag_2O+CO=2Ag+Ag_2CO_3$$

(Gautier, Compt. rend. 1898, **126**, 171). Blacet, Leighton and MacDonald (*l.c.*) confirm that no carbon dioxide is produced.

Hydrogen and other combustible Gases.—By explosion, initiated either by external heating of the inverted test-tube holding the gases, or by means of a bent tube introduced into the vessel, and containing a spark-gap, the points being filed down flush with the glass.

Slow combustion and fractional combustion may be carried out by means of a hook-shaped glass tube, through the tip of which 2 cm. of platinum wire (0·125 mm.) is fused; the tube is filled with mercury and closed so as to make contact with the platinum and with a further contact leading to the battery, the circuit being completed by the free end of platinum wire dipping into the mercury in the trough (Ambler and Sutton; Blacet and Volman, *l.c.*). A compensator for variations in temperature and barometric pressure is obtained by the use of a second horizontal tube standing in the same air-jacket as the measuring tube, the mercury-level in the trough being adjusted to give a constant volume of air in this second tube.

Movement of the gas sample in the capillary measuring tube can be easily and finely controlled by means of a screw clip which compresses a closed piece of rubber tubing attached to the other end of the measuring-tube. Speed of working and accuracy attainable are of the same order as with the macro-methods. Manipulative technique, although radically different, is not inherently more difficult, but rather the reverse, and the method may therefore be regarded as suitable for general use, even where large samples of gas are available.

Special Methods for Individual Gases.

The foregoing methods apply only to certain gases to which the volumetric method is applicable, and then only when they are present in appreciable amount, about 0·1% being about the usual limit of measurement in a general analysis. For circumstances which fall outside the above categories, methods are summarised below under the head of the individual gases. For details of such processes, it will be necessary to consult the text-books or the original papers.

Acetylene. — *Detection.* — Ammoniacal cuprous chloride, decolorised by hydroxylamine, gives a red colour due to Cu_2C_2. The reagent can be used in liquid or in test-paper form. About 0·0005% is detectable (Pietsch and Kotowski, Z. angew. Chem. 1916, **29**, 341). For quantitative colorimetric tests, parallel tests should be carried out, using known quantities of acetylene. The same reaction can be used for the determination of larger quantities by filtering off and washing the cuprous acetylide precipitate, dissolving it in acidified ferric sulphate and titrating ferrous iron; the reaction is

$$Cu_2C_2+Fe_2(SO_4)_3+H_2SO_4 =2FeSO_4+2CuSO_4+C_2H_2$$

(Willstätter and Maschmann, Ber. 1920, **53** [B], 939); *see also* Vol. I., p. 96.

Purity.—Nitrogen, etc., can be determined by absorbing the bulk of the acetylene in acetone, 1 vol. of which dissolves about 30 vols. of acetylene.

Acetone Vapour.—By conversion into iodoform with alkaline $N/10$ iodine, which is afterwards acidified and excess iodine titrated (Elliott and Dalton, Analyst, 1919, **44**, 132).

Ammonia.—The usual method of determination is titration with sulphuric acid; the indicator should be methyl-red, methyl-orange or, if the liquid is too dark, fluorescein, the end-point in this case being the appearance or disappearance of fluorescence. The gas is either passed through excess of acid, and the excess titrated with alkali, or a process similar to the Reich-Lunge method (*see under* Sulphur Dioxide) used. For small quantities of ammonia, the usual method is the colorimetric Nessler test. Aliphatic amines are determined by titration in the same way as ammonia; their effect on Nessler reagent is much less.

Argon and other Inert Gases.—For separation from nitrogen, *see* Nitrogen. For mixtures of inert gases, only physical methods of analysis are available; methods of density, thermal conductivity and fractional condensation are the most applicable (*q.v.*).

Arsine.—*Detection.*—The most sensitive test is the Marsh test (*see* p. 573). Mercuric chloride test papers (dry, made from 5% solution) give a yellow-brown colour, turned black by ammonia. Arsine may be determined gravimetrically by adsorption with heated copper (Evans, Analyst, 1920, 45, 8).

Benzene.—*Detection.*—0 02% in air gives a brown colour with a small layer of alcohol on sulphuric acid containing 0 03% of formalin (Dietrichs, Chem. Fabr. 1932, 5, 11).

Determination.—(i) Absorption and combustion methods have been described above. (ii) By nitration to *m* dinitrobenzene ("Technical Gas Analysis," p. 267). For colorimetric nitration methods, *see* Gavrilov (1932, B. 536); Smyth (*ibid* 1930, 265); Schrenk, Pearce and Yant (U S Bur. Mines, Rept. Invest. 1936, No. 3302((iii) By adsorption with active charcoal at ordinary temperatures (Berl, Andress and Muller, Z angew. Chem. 1921, 34, 125; Gregory, Oil Gas J., 1935, 33, No. 36, pp. 14, 45). (iv) By condensation at $-80°C$. (Lunge and Ambler, *op cit.*, p. 169) (v) By physical methods, particularly thermal conductivity, the viscosity-effusion bridge, refractivity and absorption spectra (p. 685).

Bromine.—*Detection.*—Colorimetrically, by absorption with magenta, decolorised by sulphurous acid and mixed with an equal volume of acetic acid (Denigès and Chelle, Bull. Soc. chim. 1913 [iv.], 13, 626).

Carbon Dioxide.—(i) *Pettenkofer's Method.* Small proportions in air, etc, are conveniently determined by absorption in lime water or baryta, the excess of which is titrated with hydrochloric or acetic acid (phenolphthalein or thymolphthalein indicator). The air is taken in a dry flask of about 1 litre capacity, and a known volume of the alkali (0 04*N*) added up to about four times the equivalent of the amount of CO_2 expected After about 20 minutes (for high accuracy some hours) the contents of the vessel are titrated. A parallel blank experiment with CO_2-free air should be carried out: 1 ml. *N*/10 lime water or baryta is equivalent to 1·119 ml. CO_2 at *N.T.P.* Similar methods, using alcoholic sodium carbonate have been described by Winkler (Z. anal Chem 1933, 92, 23; 1935, 100, 29) For a colorimetric adaptation of this method, *see* Kauko and Yli-Uotila (1936, B 493).

(ii) *Gravimetric Methods*—An alkaline adsorbent is used, preferably one of the special preparations such as "Ascarite," "Carbest," "Soda-Asbestos," etc.

(iii) *Physical Methods* (p. 685 *et seq*)—A variety of these, such as thermal conductivity, are used for indicating and recording CO_2 in flue gases, etc.

Carbon Monoxide.—*Detection.*—Numerous methods for the detection and determination of small quantities of CO have been worked out, many in great detail. Some of these are summarised below; fuller particulars are given in Lunge and Ambler, *op cit.*, pp. 226–240.

(i) *Palladium Test.*—Solutions of palladous chloride, $PdCl_2$, are reduced at ordinary temperatures, giving metallic palladium; it is generally used in the form of test-papers, which should be employed in the damp state. The $PdCl_2$ is dissolved in water, acetone and water, or aqueous NaCl, KCl or NH_4Cl The method has been studied by Daller (Z. anal. Chem. 1935, 103, 83). Quantitative methods based on this reaction have been worked out by Winkler (*ibid.* 1934, 97, 18; 1935, 100, 321; 102, 99), and by Christman *et al.* (Ind. Eng. Chem [Anal], 1937, 9, 153).

(ii) *Ammoniacal Silver Oxide.*—This is rather more sensitive than palladium but cannot be used with test papers. Quantitative methods on the same principle are described by Manchot and Lehmann (Ber. 1931, 64 [B], 1261).

(iii) *Catalytic Oxidation at Ordinary Temperatures.*—"Hopcalite" is a preparation of metallic oxides which catalyses the combustion of carbon monoxide with oxygen at ordinary temperatures; hydrogen is not affected unless amounts of carbon monoxide are excessive (0 5%). The CO is determined either by determination of the resulting CO_2 or, as in some automatic instruments, by devices controlled by the heat evolved by the oxidation (*see* Electrician, 1933, 111, 309, Frevert and Francis, Ind. Eng. Chem. [Anal.], 1934, 6, 226).

(iv) The most accurate and sensitive method for the determination of carbon monoxide in very small quantities is the reaction with iodine pentoxide at 120°–200°C:

$$5CO+I_2O_5=5CO_2+2I\ ,$$

the CO is measured either by collection of the resulting carbon dioxide, or, more sensitively, by measurement of the resulting iodine; if the CO content exceeds 0 1%, the former procedure is preferable. If hydrogen and methane are absent, it is preferable to work at 200°C.; these are, however, slightly attacked above 120°; unsaturated hydrocarbons interfere and must be removed. The most convenient way of determining the iodine is by collecting it in KI solution and titrating with thiosulphate, or preferably sodium arsenite. Quantities of the order of $1\mu g.$ of CO can be detected, and there is no limit to the amount of sample which may be taken for the purpose.

(v) *Blood Test.*—The most specific test for carbon monoxide is the blood test. A convenient and very precise method of applying this is by means of the Hartridge Reversion Spectroscope (*see* Frederick, Analyst, 1931, 56, 561), which measures the mean wave-lengths of the carboxyhæmoglobin bands in the absorption spectrum of blood which has absorbed CO; the measurement gives both a specific indication of CO and a quantitative figure. For the determination of the *purity* of CO, *see* Ambler and Sutton, Analyst, 1934, 59, 809.

Carbon Disulphide.—*Detection.*—If the gas is passed through alcoholic potash, the alcohol distilled off, the residue acidified with acetic acid and copper sulphate added, yellow copper xanthate is produced. The same reaction is used quantitatively by filtering, and determining the excess copper in the filtrate (Harding and Doran, J. Amer. Chem. Soc. 1907, 29, 1476) or by titrating with iodine without adding copper (Matuszak, Ind. Eng. Chem. [Anal], 1932, 4, 98). Diethylamine and copper acetate give a

yellow colour which provides a very sensitive test (Tischler, *ibid.* p. 46), which can be used with test papers (Kusnetzow, Z. anal. Chem. 1933, **95**, 170). For a colorimetric method with piperidine, *see* J.S.C.I. 1937, **56**, 287.

Carbon Oxysulphide, COS.—Starch solution coloured blue with a trace of iodine changes to violet and then to red, the colour finally disappearing; COS can be determined volumetrically by virtue of the fact that it is easily soluble in dilute alkali, but only very slowly in concentrated alkali (Stock and Kuss, Ber. 1917, **50**, 159).

Chlorine.—*Detection.*—The most sensitive test is a 1% solution of *o*-tolidine in 10% HCl (Ellms and Hauser, Ind. Eng. Chem. 1913, **5**, 915; Porter, *ibid.* 1926, **18**, 730). Chlorine is usually determined quantitatively by passing the gas through potassium iodide solution and titrating the liberated iodine.

Cyanogen.—*See* Hydrogen Cyanide.

Ethane.—*See* Methane.

Ethyl Alcohol.—By oxidation to acetic acid with chromic acid, and iodometric determination of the excess chromic acid (Szeberényi, Z. anal. Chem. 1915, **54**, 409; Elliott and Dalton, Analyst, 1919, **44**, 132).

Ethyl Ether.—By oxidation with iodine pentoxide at 200°C.; 5 mols. of ether liberate 24 atoms of iodine (Haggard, J. Biol. Chem. 1923, **55**, 131).

Ethylene.—Small quantities of ethylene and other olefines are determined by shaking the gas with *N*/10-bromine water (or bromate-bromide solution). The excess bromine is determined by adding excess iodide and determining the iodine. Benzene does not interfere (Haber and Oechelhäuser, J. Gasbeleucht. 1900, **43**, 34) and acetylene very little if at all.

Ethylene Oxide.—Concentrated NaCl or $MgCl_2$ reacts with this gas giving alkali, which is titrated. For details, *see* Lubatti, J.S.C.I. 1932, **51**, 361; 1935, **54**, 424; Deckert, Z. angew. Chem. 1932, **45**, 559; Chem. Age, 1935, **32**, 355; Kerckow, Z. anal. Chem. 1937, **108**, 249.

Helium.—*See* Argon.

Hydrogen.—*Detection and Determination of Small Quantities.*—(i) Volumetric determination. Some special instruments have been designed for small quantities of hydrogen in air, etc.; the limit of measurement is about 0·01% on the total gas. (ii) Conversion to HCl. By passing the gas over dry palladium chloride (Phillips, Amer. Chem. J. 1894, **16**, 259) or by mixing it with chlorine gas, the excess chlorine being removed by silver gauze (Heyne, Z. angew. Chem. 1927, **70**, 179). (iii) By passing the gas over platinum gauze immersed in sodium molybdate solution; the molybdate gives a blue colour (Zenghelis, Z. anal. Chem. 1910, **49**, 729). (iv) Spectroscopically, 0·005% in nitrogen or an inert gas is detectable at 0·05–0·08 mm. pressure. (v) Absorption of other gases by cooled silica gel. At liquid-air temperatures, all gases except hydrogen (and helium and neon) are absorbed (Lebeau and Marmasse, Compt. rend. 1926, **182**, 1086).

Purity.—Oxygen is determined by combustion (p. 679); methane by combustion after removal of hydrogen by copper oxide; nitrogen, etc., by measurement of the residual gas after combustion with copper oxide.

Hydrogen Chloride.—By absorption in alkali and titration, or gravimetrically as silver chloride.

Hydrogen Cyanide and Cyanogen.—*Detection.*—These are both readily absorbed by alkali solution, cyanogen giving equal quantities of cyanide and cyanate. The only entirely specific test for cyanides is the Prussian-blue test. For this, the alkaline solution containing the cyanide is shaken with precipitated ferrous hydroxide and allowed to stand for 30 minutes, it is then acidified and a ferric salt added (there is usually enough present produced by oxidation). The Prussian-blue precipitate can be determined by weighing as $[Fe_7(CN)_{18}, c.\ 9H_2O]$, by washing into a flask and titrating with alkali until the disappearance of the blue colour (Nauss, J. Gasbeleucht. 1900, **43**, 696), or colorimetrically. For the detection of very small quantities (down to 2 mg. per litre) the amount of ferrous hydroxide must be very small (10 mg.) and it is advisable to filter before acidification, and add only a trace of ferric salt. Quantitative colorimetric determination of these small quantities by this means requires great care, as the density of colour of the suspended precipitate depends greatly on the presence of electrolytes; these must be kept as low as possible, and comparison tests carried out under precisely similar conditions. The process is dealt with in detail by Kolthoff (Z. anal. Chem. 1918, **57**, 1). One of the most satisfactory colorimetric tests for small quantities of hydrogen cyanide is a test paper impregnated with a mixture of copper acetate and benzidine acetate (Sieverts and Hermsdorf, Z. angew. Chem. 1921, **34**, 3; Deckert, J. Desinfektion, 1930, **22**, 81). The solution is made by mixing, immediately before use, equal volumes of solutions of copper acetate (2·9 g. per litre) and benzidine acetate (48 ml. of saturated solution made up to 100 ml.). The test is quantitative for gases containing down to 0·0005% of hydrogen cyanide. For other tests for small quantities, *see* Kolthoff (*l.c.*) and Lunge and Ambler, *op. cit.*, pp. 292–297.

Hydrogen cyanide, but not cyanogen is absorbed by weakly acidified silver nitrate; this serves as a method of separate determination of the two gases. For other methods of quantitative determination of HCN, *see* Seil (Ind. Eng. Chem. 1926, **18**, 14), Brender-à-Brandis and Bohlken (Het Gas, 1933, **10**, 194), Page and Gloyns (J.S.C.I. 1936, **55**, 209), and Lunge and Ambler, *op. cit.* For determination of HCN in presence of HCl, HBr, and HI, *see* Polstorff and Meyer (Z. anal. Chem. 1912, **51**, 601).

Hydrogen Sulphide.—*Detection.*—About 0·002% in air is detectable by smell; above about 0·1% the characteristic smell alters and becomes less distinctive. The most convenient and most sensitive qualititative test is lead acetate paper; dry papers are satisfactory. It can be determined gravimetrically by absorption with copper sulphate, copper phosphate (Wright, J.S.C.I. 1885, **4**, 665) or cadmium chloride (Harding and Johnson, Ind. Eng. Chem.

1913, 5, 836). It can also be determined by titration with iodine according to the equation

$$H_2S+2I=2HI+S$$

Colorimetric methods have been worked out by Harcourt ("Technical Gas Analysis," p. 246), Winkler (Z. anal. Chem. 1913, 52, 641), and Clarke (Analyst, 1931, 57, 436). Hydrogen sulphide and sulphur dioxide can co-exist in small proportions; for determination of these together, *see* Votoček (Ber. 1907, 40, 414) and Böeseken and Muller (Rec. trav. chim. 1931, 60, 1117).

Lead Tetraethyl.—*See* Lunge and Ambler, *op. cit.*, p. 309.

Mercaptan.—This gives a yellow colour with lead acetate. *See also* Reith, Rec. trav. chim. 1934, 53, 18.

Mercury Vapour.—This can be condensed by passing the air or gas through a tube cooled in liquid air, or absorbed by bromine water (Moldawski, Chem. Zentr. 1931, i, 1644). The mercury is then determined by a microscopic method (*see* Stock and Cucuel, Ber. 1934, 67, 122).

Methane.—This is determined in air by combustion with oxygen over heated platinum or palladium and volumetric measurement. A large number of instruments on this principle have been described. Very small proportions can be determined by carrying out the combustion in a flask in the presence of standard lime water or baryta, and determining the resulting carbon dioxide by titration. For small quantities of methane in the presence of large quantities of hydrogen and carbon monoxide, *see* Ambler, Analyst, 1932, 56, 635 Methane is the only hydrocarbon which is not condensed at liquid air temperature to a substance of negligible vapour pressure (*v.*, p. 686), it is also by far the lightest hydrocarbon, and can thus be determined by density measurements (p. 686). The gas interferometer (p. 687) can detect 0·01% in air

Higher paraffins are in general determined in similar ways to methane; there are no chemical methods of separation, but physical processes are available (p. 686).

Methanol.—By oxidation to formaldehyde by means of permanganate, and determination of formaldehyde with a modified Schiff reagent (Jephcott, Analyst, 1935, 60, 588)

Nitric Oxide.—This can be determined volumetrically by absorption with ferrous sulphate (30%); two successive portions of reagent being used as with cuprous chloride. NO in small proportions is usually detected and determined together with the trioxide and tetroxide by the Griess test. It is oxidised to nitric acid by acid (sulphuric) hydrogen peroxide, the nitric acid being determined colorimetrically with phenoldisulphonic acid (Francis and Parsons, Analyst, 1925, 50, 262). For methods of discrimination between the various constituents of "nitrous fumes," *see* Sanfourche and Bureau (Compt. rend. 1936, 202, 60). *See also* Nitrogen Dioxide.

Nitrogen.—In ordinary gas analysis, nitrogen is nearly always determined by difference. Where the nitrogen content is of especial importance, the separate determination of the other gases, and the accumulated error so introduced, may be obviated by removing them in one process, either by means of copper oxide at c. 1,000° (Evans, Gas World, 1911, 55, 814) or by burning with electrolytic oxygen and absorbing the excess (Ambler, Analyst, 1931, 56, 804). Nitrogen is determined chemically only where argon and its congeners are to be determined; the most efficient adsorbent is lithium at 300° (Trautz and Kipphan, Z. anal. Chem. 1929, 76, 350; Copaux, Bull. Soc. chim. 1932 [v], 51, 989; Severyns, Wilkinson and Schumb, Ind. Eng. Chem. [Anal.], 1932 [v], 4, 357). Small proportions of nitrogen in argon are detectable by their inhibiting effect on the characteristic argon spectrum. See Vol. I., p 465

Nitrogen Dioxide (NO_2 and N_2O_4).—This is usually determined by conversion to nitrite or nitrate; for a volumetric determination (at 156°C), *see* Whittaker, Lundström and Merz, Ind. Eng. Chem. [Anal.], 1930, 2, 15. Very small quantities are determinable by absorption spectrum methods (p. 687).

Nitrous Oxide.—This is perhaps the most difficult of all gases to determine chemically; owing to its appreciable solubility in all liquid reagents, its presence makes ordinary absorption methods for other gases impracticable. No known reagent, however, will absorb it completely. In the absence of oxygen, it can be determined volumetrically by reduction with hydrogen, either by explosion or with heated platinum wire, in the explosion method the H_2/N_2O ratio must be between 1·8 and 2·5 (Menzel and Kretzschmar, Z angew. Chem. 1929, 42, 148) With platinum, the temperature must be kept below 500°, or some ammonia may be produced (*l.c.*); this is obviated if CO is used instead of hydrogen. For determination of N_2O and oxygen together, by combustion with CO, *see* Lunge and Ambler, *op. cit.*, p. 275. Oxygen in nitrous oxide may be determined by adsorption with damp phosphorus confined over mercury (Menzel and Kretzschmar, *l.c.*; Ambler, Analyst, 1934, 59, 14), but some N_2O may be decomposed in the process. With complicated gas mixtures, or small proportions of N_2O, the only accurate method of determination is condensation with liquid air. Density, thermal conductivity and refractivity (p 685) measurements are of great use with mixtures of known qualitative composition. For the routine examination of nitrous oxide in cylinders, *see* Bennett (J. Physical Chem 1930, 34, 1137), and Chaney and Lombard (Ind. Eng. Chem [Anal.], 1932, 4, 185).

Organic Vapours.—Where it is not needed to determine individual organic vapours, combustion methods with platinum wire are rapid and convenient; any sufficiently sensitive gas analysis apparatus fitted with platinum wire combustion apparatus is suitable. A special instrument for the purpose has been described by McNair and Gull (Analyst, 1932, 57, 159).

Oxygen.—*Volumetric Combustion Methods*—Combustion with hydrogen under the influence of platinum wire is a convenient and very accurate method; in the presence of carbon monoxide the accuracy is reduced to about 0·1% (Ambler, Analyst, 1930, 55, 677). De Voogd

and Bohlken (Het Gas, 1934, 54, 43) have used the same principle for oxygen in coal-gas; unsaturated hydrocarbons apparently do not seriously interfere (*l.c.*).

Colorimetric Tests.—The most convenient colorimetric test is with alkaline pyrogallol; the colour is matched with iodine solution (Pfeiffer, J. Gasbeleucht. 1897, 40, 354; Ambler, Analyst, 1934, 59, 14). The most sensitive test is probably that with a ferrous salt and alkaline catechol (Binder and Weinland, Ber. 1913, 46, 255).

Purity.—By absorption with ammoniacal copper (Frederick, Analyst, 1935, 60, 581); in the writer's experience, hydrogen and methane are not perceptibly affected by this reagent.

Ozone.—*Detection.*—Potassium iodide–starch or preferably potassium iodide–phenolphthalein papers; these tests are not, however, entirely specific. The most satisfactory chemical quantitative method is absorption with potassium iodide and titration of the iodine, the hydrogen-ion concentration being kept constant with a buffer solution (Juliard and Silberschatz, Bull. Soc. chim. Belg. 1928, 37, 205; Ruyssen, Natuurwetensch. Tijds. 1933, 15, 125). Ozone is also determined by the absorption-spectrum method (p. 687) (Ruyssen, *ibid.* p. 6).

Phosgene (Carbonyl Chloride).—*Detection.*—Test-papers made from a solution of 1 g. *p*-dimethylaminobenzaldehyde and 1 g. diphenylamine in 5 ml. absolute alcohol give a yellow colour with about 0·0001% of phosgene (Suchier, Z. anal. Chem. 1929, 79, 183).

Determination.—(i) By conversion to diphenylurea by absorption in aqueous aniline (Olsen *et al.*, Ind. Eng. Chem. [Anal.], 1931, 3, 189; Yant *et al.*, *ibid.* 1936, 8, 21). (ii) By absorption in a 2% solution of sodium iodide in acetone, and titration of the iodine produced (Olsen *et al.*, *l.c.*). *See also* Matuszak, *ibid.* 1934, 6, 457.

Phosphine.—*Detection.*—Silver nitrate test papers are blackened; the test is not specific, however. Bromine-water or hypochlorite gives phosphoric acid. For further methods, *see* Lemoult, Compt. rend. 1904, 139, 478; Wilmet, *ibid.* 1927, 185, 206.

Sulphur Dioxide.—This is usually determined by titration. In the Reich-Lunge method (Lunge and Ambler, *op. cit.*, p. 152) the gas under test is bubbled through a litre bottle half filled with water containing 10 ml. of N/10-iodine and starch, until the blue colour disappears. The volume of gas passed is then measured by the volume of water displaced from the aspirator used to draw the gas. The reaction is:

$$SO_2+2I+2H_2O=2HI+H_2SO_4$$

For very small quantities of SO_2 in air, *see* Griffin and Skinner, Ind. Eng. Chem. 1932, 24, 862. *See also under* Sulphur Trioxide.

Purity.—Gases which are not soluble in alkali, by absorption of SO_2 with alkali and analysis of the residue; CO_2, by removal of SO_2 by dichromate, and gravimetric determination of CO_2; water, gravimetrically by absorption by phosphorus pentoxide (Scribner, Ind. Eng. Chem. [Anal.], 1931, 3, 255). Sulphur dioxide for preservative purposes is tested for traces of arsenic by a Marsh test on the residue after evaporating off the sulphur dioxide.

Sulphur Trioxide.—In the absence of SO_2, this is determined by absorption in standard alkali; the gas is either passed until the end-point is reached, as in the Reich-Lunge method, or excess alkali is used and is back-titrated; SO_2 and SO_3 together (*i.e.* total acid) can be determined in this way using phenolphthalein indicator, or by the Reich-Lunge method, the SO_2 being determined separately iodometrically. Mixed-indicator methods are also available (*see* Dieckmann, Analyst, 1921, 46, 517). For details of these and other methods employed in the sulphuric industry, *see* Lunge and Keane's "Technical Methods of Chemical Analysis," Vol. I, and "Technical Gas Analysis."

Total Sulphur.—For control purposes in gas works, etc., it is often sufficient to determine total sulphur without separate determination of the various gaseous sulphur compounds. The general method is to burn the gas in excess of oxygen and determine the total sulphur as sulphate. The usual method in this country is known as the Referees' method, and is described in the "General Notification of the Gas Referees" for 1918. The burnt gases are passed through solid "sesquicarbonate of ammonia," the sulphur being collected as ammonium sulphate and determined gravimetrically. *See also* Lieber and Rosen, Ind. Eng. Chem. [Anal.], 1932, 4, 90.

Water Vapour.—Water vapour is most simply determined by passing a known volume of the gas through a weighed tube containing phosphorus pentoxide or other suitable adsorbent. It can also be determined volumetrically, using a dry measuring apparatus and absorbing the water vapour with sulphuric acid (Blackie, J. Sci. Instr. 1936, 13, 6). Small quantities can be determined by the reaction with calcium hydride, which liberates hydrogen quantitatively (Hackspill and d'Huart, Ann. Chim. 1926, 5, 95). Physical methods such as the wet-and-dry bulb thermometer are largely used (*see* Hyde and Mills, "Gas Calorimetry," p. 338).

Physical Methods.

Physical methods of gas analysis fall into two general classes: (i) those in which the constituents are *separated* from one another by virtue of differences in such properties as volatility or selective adsorption by charcoal, and (ii) those in which the relative proportions of constituents are determined without separation by the measurement of some physical constant of the mixture, such as density or refractivity. In general, methods of this latter class are applicable only to binary mixtures of known qualitative composition. They usually require calibration with mixtures of known composition. For regular control analyses of simple mixtures, however, speed and simplicity of technique make such processes of increasingly wide technical importance.

Condensation Methods.—The simpler condensation methods are those where constituents are separated into two fractions by the complete condensation of one constituent or group of

constituents, the other fraction remaining wholly gaseous. An example is the separation of methane from other paraffins at the temperature of liquid air. All other hydrocarbons are condensed at this temperature to liquids or solids of negligibly small vapour pressure, while that of methane is sufficiently high (approximately 20 mm.) for it to be completely removed from the other gases by pumping. At $-185°C.$ the only common gases which are not condensed to substances with negligible vapour pressures are hydrogen, nitrogen, oxygen, carbon monoxide, nitric oxide and the inert gases. An analysis of a complex mixture may be greatly simplified by removing in this way all condensable gases preparatory to a general analysis of the non condensable residue. At approximately $-80°$ the temperature attained by mixtures of solid carbon dioxide with ether, acetone, etc., all vapours such as benzene, etc., can be removed from such substances as are gaseous at ordinary temperatures. Processes on these general lines have been described by Burrell, Seibert and Robertson (U.S. Bur. Mines Tech. Paper, No. 104; Bur. Mines Bull. 197); Stockings and Himus, "Fuel Testing," 1932, p. 195; Lebeau and Damiens (Compt. rend. 1913, 156, 325); Whiton (Ind Eng. Chem. 1916, 8, 735). For more complicated mixtures, the use of vacuum jacketed fractionation columns has made the separation of the constituents of a complex mixture almost as simple as the fractional distillation of organic liquids. The constituents distil over almost completely separated, and are identified by their boiling-points and measured by the collection of each constant-boiling fraction in a previously evacuated vessel of known volume, connected to a manometer. For details of the most modern processes, *see* Podbielniak (Ind. Eng. Chem [Anal.], 1931, 3, 177; 1933, 5, 119, 172), MacGillivray (J C.S. 1932, 941); McMillan (J. Inst. Petroleum Tech 1936, 22, 616) and Rose (Ind. Eng. Chem. [Anal], 1936, 8, 488) For binary and ternary mixtures of known qualitative composition, a simpler and more rapid process has been worked out in which the fractionation column is dispensed with (Rosen and Robertson, Ind Eng. Chem. [Anal.], 1931, 3, 284; 1934, 6, 12); the temperatures are noted at which certain specified percentages of the total gas have been evaporated off under standardised conditions, and from these data the composition is obtained from empirically constructed graphs. For small samples of gases and vapours, there is an ingenious and interesting process in which the increase of vapour pressure of the condensed gas with a slowly rising temperature is measured at a low total pressure by means of the Pirani gauge. Each constituent has a typical curve of this type by which it can be identified, and the total rise of pressure on complete evaporation is the measure of its amount. It is found that there is very little interference between different constituents. For details, *see* Research Staff, G.E.C. (Proc. Physical Soc. 1921, 33, 287) and Sebastian and Howard (Ind. Eng. Chem. [Anal.], 1934, 6, 172).

Adsorption by Charcoal and Silica Gel.—The adsorptive power of cooled charcoal or silica gel varies greatly for different gases, and, if the amount of adsorbing substance is limited, is highly selective. At temperatures of liquid air, all gases except helium, hydrogen, and to some extent, neon, are so firmly adsorbed by active charcoal or silica gel, that they are not removed by evacuation. Helium is the least adsorbed of all gases, and can be separated almost quantitatively by this means from all gases but hydrogen and neon (McClennan, J.C.S. 1920, 117, 943; Paneth and Peters, Z. physikal. Chem. 1928, 134, 353. For other references, *see* Lunge and Ambler, *op. cit.*, p. 177). Processes for the analysis of complex hydrocarbon mixtures by selective adsorption in charcoal or silica gel have been described by Schuftan "Gasanalyse in der Technik," p. 69, Berl and Schmidt (Z. angew. Chem. 1923, 36, 247), Kuhn (*ibid.* 1931, 44, 757), and Peters and Lohmar (Brennstoff-Chem. 1937, 18, 41).

Density.—Density measurements provide a convenient and absolute method for the analysis of simple mixtures, and for check tests on general analyses. They are particularly useful with the inert gases and with hydrocarbon mixtures. Convenient methods of measuring densities of gases are: (i) Density balances (Hales and Moss, J. Sci. Instr. 1935, 12, 309; Edwards, U.S. Bur. Stand. Tech. Paper No. 89). (ii) Static column method, in which the hydrostatic pressure of a column of gas is measured by a sensitive manometer; the process is simple and accurate, the sensitivity depending on that of the manometer available and on the height of the column Processes on this principle have been described by Krell (J. Gasbeleucht. 1899, 42, 212), Threlfall (J.S.C.I. 1907, 26, 359), Pollitzer (Z. angew. Chem. 1924, 37, 459) and Blackie (Fuel Research Tech. Paper No. 5). In the experience of the present writer, small samples (2 ml.) can be tested with considerable accuracy, using columns of 1 mm. bore. (iv) Effusion methods, in which the time taken for a volume of gas to pass through a small orifice is measured; these methods are convenient but are not absolute; critical examinations of the method have been made by Edwards (U.S. Bur Stand. Tech Paper No. 94), and by Kemp, Collins, and Kuhn (Ind. Eng. Chem. [Anal.], 1935, 7, 338). (v) Velocity of sound (Geberth, Ind Eng. Chem. 1923, 15, 1277; Griffiths, Proc. Physical Soc. 1927, 30, 300) (vi) Various automatic indicators and recorders, working on a variety of principles, have been designed and are described by Levy, "Gasworks Recorders," 1928.

Thermal Conductivity.—This method is becoming increasingly used for control analyses in industry in view of its natural advantages of cleanliness, reliability and adaptability to automatically-recording "flow" processes. The principle of the method is that a wire, heated by an electric current, loses heat in proportion to the thermal conductivity of the gas surrounding it; hence, for a given current, its temperature, and consequently its electrical resistance, is a function of the thermal conductivity, and hence of the composition of the surrounding gas. The resistance is measured by making the wire one arm of a Wheatstone

bridge. The method is widely used with flue gases for the continuous recording of carbon dioxide. The applications of the method to gas analysis and very full practical details are given by Daynes, "Gas Analysis by Measurement of Thermal Conductivity," 1933, and also by Palmer and Weaver (U.S. Bur. Stand. Tech. Paper No. 249). The same principle has been used for very small quantities (0·005 ml.) of mixtures involving H_2, D_2, and HD and of mixtures of ortho- and para-hydrogen (Bolland and Melville, Trans. Faraday Soc. 1937, **33**, 1316; Twigg, *ibid.* 132).

Viscosity.—The direct measurement of the viscosity of a gas mixture is little used as an analytical method. In some cases, however, where only very small samples are available, it may be useful since samples of the order of 1 ml. can be examined with high precision by the method of Rankine (Proc. Roy. Soc. A, 1910, **83**, 265; **84**, 181). For practical purposes the viscosity-effusion bridge (Fagelston, Ind. Chem. 1932, **8**, 57), which depends on the relation between the density and viscosity of a gas, offers a highly sensitive method of determining small proportions of some gases, especially organic vapours, which have high densities and low viscosities; by means of a combination of capillary tubes and effusion orifices, arranged something like the arms of a Wheatstone bridge, small differences in the density-viscosity ratio between the gas under test and a comparison gas are indicated on an oil-manometer. The design of the apparatus allows it to be used with corrosive gases.

Refractivity.—The index of refraction of all gases is very close to unity; by means of the gas interferometer (Lord Rayleigh, Proc. Roy. Soc. 1896, **59**, 201; 1898, **64**, 97), however, differences in this quantity can be measured with extreme sensitiveness, with the result that as little as 0·01% of hydrogen in air can be measured, although the extent to which the refractive index is thus affected is only 15×10^{-9}. The method can deal with small samples and is rapid in working. The gas under test and a comparison gas are contained in two parallel tubes of about 1 metre length; the light passing through the two tubes is made to produce interference bands in the two halves of the visual field. When the refractivities of the gases are equal, the bands coincide; when they differ, they are brought together by rotating a graduated drum, from the reading on which the difference in refractivity is obtained. For details, *see* Edwards (U.S. Bur. Stand. Tech. Paper No. 113; J. Amer. Chem. Soc. 1917, **39**, 2382); Burrell and Seibert (U.S. Mines Bull. No. 14); Seibert and Harpster (U.S. Bur. Mines Tech. Paper No. 185); Kershaw (Chem. Met. Eng. 1919, **20**, 291). The method has been used for the determination of methane in mine air; portable instruments have been made for this purpose, with a sensitivity of about one-tenth of the laboratory apparatus.

Spectroscopic Methods.—*Emission Spectra.*—The sensitiveness of spectroscopy as a method of gas analysis varies greatly according to the gas under test; it is of high value with the gases of the argon group. For the spectroscopic determination of exceedingly small quantities of helium, *see* Paneth and Peters (Z. physikal. Chem. 1928, **134**, 353). Mixtures of krypton and xenon have been analysed quantitatively by a spectrophotometric method (Moureu and Lepape, Compt. rend. 1911, **152**, 691; 1911, **153**, 740; 1922, **174**, 908); 0·005% of hydrogen in nitrogen or inert gas can be detected spectroscopically (Heyne, Z. angew. Chem. 1925, **38**, 1099). Quite small proportions of nitrogen interfere with the argon spectrum, a fact which provides a method for its detection in this gas. For experimental details of the spectroscopy of gases, *see* Baly, "Spectroscopy," 3rd ed., 1937, Vol. II, p. 157 and Travers "Study of Gases," p. 298. Gatterer (Physikal. Z. 1932, **33**, 64) has shown the possibility of quantitative analysis of various gaseous mixtures by this method.

Absorption Spectra.—Analytical methods on this principle have been used for nitrogen dioxide (Robertson and Napper, J.C.S. 1907, **91**, 761; Willey and Foord, Proc. Roy. Soc. *A*, 1932, **135**, 166). The latter workers, using the potassium photoelectric cell, can detect 0·001% of NO_2. Lambrey (Compt. rend. 1931, **193**, 857) has used absorption spectra for the detection of nitric oxide. Other gases which can be determined in this way are ozone (Krüger and Moeller, Physikal. Z. 1912, **13**, 729; Ruyssen, Natuurwetensch. Tijds. 1933, **15**, 6), methane (Krüger, Reinkober and Riegger, Chem. Zentr. 1919, ii, 39), and benzene vapour (Laurian, 14th Congress of Chemistry and Industry, Paris, 1934; Gull and Martin, J. Sci. Instr. 1935, **12**, 379). *Raman spectra* have been applied to the determination of olefines in the presence of trimethylene derivatives (Lespieau, Bourguel and Wakeman, Compt. rend. 1931, **193**, 238).

H. R. A.

GAS-VOLUMETRIC METHODS OF ANALYSIS

The above term is applied to those processes in which a solid or liquid substance is determined by the generation and measurement of a gas. The *nitrometer*, devised by Lunge (Ber. 1878, **11**, 434; 1888, **21**, 376; 1895, **28**, 1878, 2030) for the estimation of nitric acid and nitrates, is applicable to a large number of other purposes of this type. It consists (Fig. 9) of a burette, fitted at the top with a three-way tap and cup-shaped funnel, and communicating at the bottom, by means of rubber tubing, with a levelling-tube of the same diameter. To increase accuracy, the volume may be increased by expanding the upper part into a bulb as shown in Fig. 10. The use of the nitrometer for the determination of nitrates is based on the fact that when a nitrate solution is shaken with concentrated sulphuric acid in the presence of mercury, the nitrogen is given up as nitric oxide. For the analysis of, say, nitrous vitriol, the apparatus is filled with mercury, so that when the tap is open, mercury just passes into the funnel when the levelling-tube is raised. The nitrous vitriol is now introduced into the funnel (0·5–5 ml., according to strength), the levelling-tube lowered and the vitriol drawn into the nitrometer, care being taken to admit no air. The funnel is now rinsed with 2–3 ml. of sulphuric

acid which is similarly drawn into the burette, and the process repeated with a further 1–2 ml. The burette is now removed from its clamp, and the reaction brought about by vigorously shaking the acid and mercury together. When no further gas is evolved, the tubes are levelled; 1 mm. of mercury is taken as equivalent to 6·5 mm. of acid. The final levelling is done by cautious opening of the tap with a small quantity of acid in the funnel. The volume is now read, also the barometric pressure and the temperature in the immediate neighbourhood of the middle of the column of gas. The volume is reduced to *N.T.P.* and (in the absence of further corrections, *q.v.*) 1 ml. of NO is taken as equivalent to 0·625 mg. N or 2·813 mg. HNO_3. This uncorrected figure is adequate for most purposes; for high precision work, various corrections are applied on account of physical solution of nitric oxide, formation of ammonia, nitrogen, nitrous oxide, etc. Detailed studies of such effects have been made by Newfield and Marx (J. Amer. Chem. Soc. 1906, 28, 877), Marqueyrol and Florentin (Bull. Soc. chim.

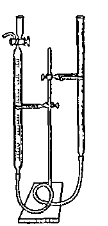

FIG. 9.

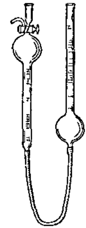

FIG. 10.

1911, 9, 234), Beckett (J.C.S. 1920, 117, 220), and Marqueyrol (Mém. Poudres, 1924, 21, 326). For substances soluble in water, a small quantity of aqueous solution is drawn into the tube, and the funnel washed out with the strong acid; substances insoluble in water (*e.g.* nitrocellulose) are dissolved in the funnel.

The nitrometer may be used for almost any reaction in which a gas is quantitatively evolved; important applications are the determination of (i) ammonia, urea and other amino-compounds with hypobromite, (ii) carbonates, (iii) hydrogen peroxide and other oxidising substances, by reaction with excess of permanganate, etc. (Baumann, Z. angew. Chem. 1891, 4, 135, 198, 339, 392), (iv) nitrites (Riegler, Z. anal. Chem. 1897, 36, 665), (v) nitrous acid in spent nitrating acids (Holden, J.S.C.I. 1930, 49, 220). Most of these processes are more conveniently performed with an apparatus such as the following, where the decomposition is effected in a separate vessel. The separate vessel illustrated in Fig. 11 is designed for such reactions as (i), (ii), and (iii) above; other designs are used for the reaction of nitrates with mercury and sulphuric acid.

The Gas-Volumeter.—The principle of this apparatus (Fig. 11) is the provision of a "control" tube *B* which contains an amount of gas, the volume of which at *N.T.P.* is precisely known; it is usually filled with a quantity of air, the volume of which at *N.T.P.* would be exactly 100 ml. If the levelling-tube *C* is so adjusted that the mercury-level in *B* is exactly on the 100 ml. mark, and is also levelled with that in *A*, then the gas in *A* must be under the same conditions of pressure and temperature as that in *B*, which, as has been seen, indicates a correct volume at *N.T.P.* The volume in *A*, therefore, is automatically corrected to *N.T.P.* *B* is kept dry or wet according to whether the gas in *A* is dry or wet (dry for nitrates, wet for most other purposes). The Dupont nitrometer (Pitman, J.S.C.I. 1900, 19, 983) is an instrument

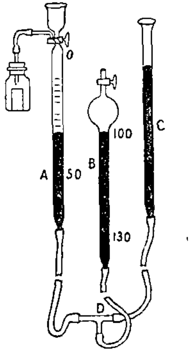

FIG. 11.

embodying this principle largely used in the U.S.A. in connection with nitrocellulose.

Schlösing-Schulze-Tiemann Method for Nitrates.—This is an important method for the determination of nitrates, in which they are converted to nitric oxide by heating with ferrous chloride and hydrochloric acid. Details of the process and the necessary apparatus are given in Treadwell and Hall's "Analytical Chemistry," Vol. II, 8th ed.; a study of its application to the analysis of nitrocellulose has been made by Marqueyrol (Mém. Poudres, 1924, 21, 326). *See also* VOLUMETRIC METHODS, p. 664. H. R. A.

ANALYTICAL APPLICATIONS OF SPECTROSCOPY.

INTRODUCTION.—For many years chemists have been familiar with the production of flame spectra of the alkali and alkaline earth metals with the aid of the visual spectroscope. The development of spectrographs with a quartz

optical system has led to the ultra-violet spectrographic analysis to all the metals and some of the non-metals. Absorption spectra have been used to a large extent in the analysis of organic compounds, but attention will be confined here to emission spectra and their use in qualitative and quantitative analysis. The chief advantages gained by the use of the spectrograph over ordinary chemical analysis are that (*a*) a few milligrams of a sample suffice for a complete analysis, (*b*) in many instances the sample need not be destroyed, (*c*) traces of impurities which might escape detection by routine analysis are easily found, (*d*) a permanent record is obtained.

METHODS OF EXCITATION.—1. *The Flame.*—The exact procedure and the mode of excitation to be adopted in any given case will depend on the nature of the material under investigation. For spectrum analysis of solutions with a flame, an ordinary Bunsen burner using town gas has too low a temperature to permit of the satisfactory volatilisation of many elements, but oxy-coal gas, oxy-hydrogen, air-acetylene and oxy-acetylene flames have been successfully used. Solutions are sprayed into the flame from specially constructed burners.

2. *The Arc.*—If the sample is in the form of a metal rod, two lengths cut from the rod are clamped in a suitable stand connected with a current supply and a direct current arc struck by touching the two electrodes. If a powder is submitted it is placed on the lower electrode of a copper, carbon or silver arc. In quantitative work particularly it is convenient to drill a small hole in the electrode and to compress the powder into a pellet which is dropped into the hole. The electrodes are brought near to one another and the arc is struck by touching both of them with a third rod of the same material. Although electrodes may be purchased specially prepared for spectroscopic analysis, they always contain small quantities of impurities, for example, the purest carbon rods often contain vanadium, iron, silicon, aluminium and titanium. Russanow (Z. anorg. Chem. 1934, **219**, 332) has shown that by heating graphite electrodes to a temperature of 2,700°C. for 3 minutes they may be freed from these elements. With this treatment, traces of calcium, boron, magnesium and copper still persist. According to Zürrer and Treadwell (Helv. Chim. Acta, 1935, **18**, 1181), the use of a flame arc with 12 ampères for 2–3 minutes in an atmosphere of hydrogen or argon with the addition of 5% of chlorine removes all elements except faint traces of calcium. In every case it is necessary to make an exposure of the electrodes as a " blank " before adding the sample. An extension of the arc method is that of the " Abreissbogen " or interrupted arc, which Gerlach states gives greater sensitivity with some elements.

3. *The Spark.*—A high-tension spark is usually to be preferred as a means of excitation if the sample is small, in the form of sheet or wire, if the material must not be destroyed, *e.g.* ancient coins, or if an exploration is to be made of differences in composition in an ingot, *e.g.* due to segregation in an alloy. The spark is conveniently obtained from a $\frac{1}{4}$ *KVA* transformer giving secondary voltages of from 8,000 to 15,000 on an open circuit. The spark gap and a condenser are shunted across the secondary of the transformer. It is found that the condenser gives an enhanced intensity to the spectral lines. A self-induction coil is inserted in the spark-gap circuit ; its use tends to eliminate air lines from the spectrum. It is convenient to have a variable condenser and a tapped self-induction coil so that the values of capacity and inductance may be varied. Two small specimens are cut and held with pincers in an insulated stand, and the condensed spark is passed between these electrodes. If the samples are small, they tend to become unduly heated and it is necessary to give intermittent exposures allowing a few seconds between successive sparkings. The utmost care must be exercised in handling the electrodes to avoid contamination.

The high-tension spark has been successfully employed also for the analysis of solutions (Twyman and Hitchen, Proc. Roy. Soc. *A*, 1931, **133**, 72), and for the investigation of the spark spectra of gases when under reduced pressure (Lundegårdh, Z. Physik, 1930, **66**, 109). Gerlach has used a high-frequency discharge from a Tesla coil for the examination of clinical and pathological samples (" Clinical and Pathological Applications of Spectrum Analysis," Adam Hilger Limited, London, 1934).

THE SPECTROGRAPH.—A number of firms have turned their attention to the manufacture of spectrographs of different sizes for various purposes. A small size allows the complete spectrum from λ 2,100 to 8,000Å to be taken on a photographic plate $4\frac{1}{4}$ in. in length. This is a convenient instrument for the study of flame and other simple spectra, *e.g.* from brasses. The " medium " size spectrograph covers the same range of wave-length on a 10-in. plate. This instrument is the most convenient size for general spectrographic work. A wave-length scale is usually incorporated in the small and medium spectrographs. This can be printed by means of a small lamp directly on to the plate in juxtaposition to the spectrogram, thus enabling the analyst to read off the wave-length of the spectrum lines. The largest spectrograph has a dispersion such that the complete spectrum would be some 25 in. in length. This dispersion is necessary for the separation of the spectral lines in steels, etc., which give complex spectra. In practice, this long spectrum is taken in three overlapping sections on a 10-in. plate, by rotating the prism and adjusting the focus of the lens and the tilt of the plate. Adam Hilger Ltd., placed on the market in 1936 an improved all-metal model of their large spectrograph. This has both glass and quartz optical trains which are interchangeable with one movement. The prisms are mounted back to back with a metal division between them. Each prism has its own lens. The range of the spectrum is altered by only one adjustment, which rotates the prism, and resets the lens and the plate. It is claimed that it is easier to take a spectrogram with this instrument than to take a photograph with a box camera. There are also simpler visual instruments suitable for

workshop use such as Hilger's Spekker Steeloscope.

INTERPRETATION OF SPECTROGRAMS.—The photographic plate containing a series of spectrum lines may be examined either by transmitted light with the aid of a low-power lens or microscope or by projection on to a translucent or opaque white screen.

"*Raies Ultimes.*"—Every element gives a characteristic spectrum of lines, the intensity of which is dependent on the method of excitation, the concentration of that element in the sample, and the presence of other elements. The simplest spectra are obtained from the flame, whilst some lines rendered visible by the spark are not given by the arc. As the concentration of an element decreases, some lines in the spectrum disappear until finally at a limiting concentration only one or two lines remain. These lines are termed the "raies ultimes" or ultimate lines; they have been investigated for almost every element (*see* Twyman and Smith "Wave length Tables for Spectrum Analysis," Hilger, London, 1931). In examining a spectrogram for a suspected element it is only necessary to look for the ultimate lines, whence its presence or absence may be directly deduced.

QUALITATIVE ANALYSIS.—The simplest method of qualitative analysis is the case

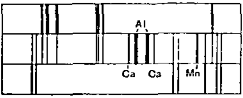

FIG. 1.

where it is known in advance which elements are to be sought. The spectrum of the test material is then photographed between the spectra of the elements whose presence is suspected. This is conveniently done by using a Hartmann diaphragm with three apertures which slides in front of the slit, *e.g.* the presence of iron and magnesium in a sample of aluminium can be confirmed by taking spectra of pure iron, the specimen of aluminium under test and pure magnesium. If the ultimate lines of iron and magnesium are seen to be coincident with lines in the aluminium spectrum, the presence of these elements is confirmed (Fig. 1). With experience, a spectroscopist knows where to look for the ultimate lines of an element and can tell by a glance at a spectrogram if a given element is present without the necessity of photographing other spectra in juxtaposition. The complete qualitative analysis of some materials may be a lengthy procedure, for example, Ramage and other workers have reported the presence of as many as fifty different elements in various samples of coal ash. The easily-identified "raies ultimes" are very useful also in the calibration of a spectrogram enabling the spectroscopist to determine the wave length of other lines present on the plate.

QUANTITATIVE ANALYSIS.—1 *Comparison Method.*—A number of different methods have been proposed. They all depend on the fact that the intensity of the spectrum lines of an element on a photographic plate is a function of the quantity of that element present in the source of light. The simplest method is the "comparison sample" method. The spectra of a series of standard alloys containing increasing known amounts of a given element are photographed, together with that of the sample, under identical conditions. The spectra are arranged in juxtaposition on the plate (Fig. 2). By visual observation of the intensity of the lines due to the impurity, an estimate may be obtained of the percentage present in the given sample. The analysis is best carried out by first using standard samples of wide range of impurity content and then repeating the analysis with other standards of narrower range determined by the previous analysis. This method of

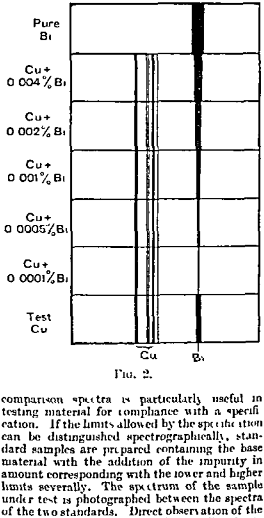

FIG. 2.

comparison spectra is particularly useful in testing material for compliance with a specification. If the limits allowed by the specification can be distinguished spectrographically, standard samples are prepared containing the base material with the addition of the impurity in amount corresponding with the lower and higher limits severally. The spectrum of the sample under test is photographed between the spectra of the two standards. Direct observation of the intensity of suitable chosen lines will indicate whether the sample conforms to the specification. In any comparative spectrographic analysis it is of the utmost importance that the technique should be carefully standardised. In using the arc, care should be taken that the current strength is maintained constant; the size of the electrodes, the arc length, the exposure and time of development should be the

same for each sample of a series. Similarly when the spark is employed, the same values of capacity and inductance should be used and the other factors maintained constant.

2. *Internal Standard Method.* — Another method of quantitative analysis which has been widely used since it was first described by Gerlach is known as the "internal standard" method. This method is based on the comparison of the intensity of a line due to an impurity with that of a line due to the base material or a known added element. Gerlach and Schweitzer ("Foundations and Methods of Chemical Analysis by the Emission Spectrum") have worked out a series of tables showing the percentage of one element in another which yields equality of intensity of "homologous pairs" of lines. The lines chosen are as far as possible those which are insensitive to change in the excitation conditions. It is nevertheless important to keep these conditions as constant as possible and, to assist in this, observation is made of another pair of lines in the spectrum of the base material one of which is an arc line and the other a spark line, the intensities of which are known to vary with the conditions of excitation. The lines are chosen to be close to one another to avoid errors due to variation of the sensitivity of the plate. The capacity and inductance in the circuit are therefore adjusted until this "fixation" pair of lines are of equal intensity. Then the analytical tables of "homologous pairs" may be directly applied. This method is obviously limited to the analysis of materials for which tables of homologous pairs of lines have been worked out.

3. *Logarithmic Sector Method.* — A more generally applicable method is that of the logarithmic wedge sector. Scheibe and Neuhäusser (Z. angew. Chem. 1928, **41**, 1218), and Twyman and Simeon (Trans. Opt. Soc. 1930, **31**, 169) have described this method in which a disc, the periphery of which is cut logarithmically, is rotated by a motor in front of the spectrograph slit. The resulting spectrum consists of a series of wedge-shaped lines (Fig. 3). The difference in length between two lines, due one to the base material and one to an impurity, is a function of the amount of the impurity present. As with the "internal standard" method, a series of standards is prepared using known percentages of one element added to a base material. A curve is drawn correlating the percentages of the added element with the differences in the lengths of two lines lying close together. The test sample is photographed under the same conditions, and from the difference in line length the percentage of the impurity is read off on the curve. With this method it is important that the whole of the slit should be evenly illuminated. This is ensured by using a condensing lens of such focal length that the image of the light source is formed on the prism of the spectrograph. A convenient datum line, from which the length of the spectrum lines is measured, is obtained by adjusting the height of the sector so that a portion of the slit is continuously exposed (*see* Fig. 3). The chief difficulty is the determination of the end-points of the lines. The lines become progressively fainter until they merge into the background. Various expedients have been suggested for measuring the line length, but the method which is most in favour consists in the use of a ×5 eye-piece fitted with a 20 mm. scale, marked with 0·1 mm. divisions. This is placed directly on the negative which is illuminated by transmitted light. With practice, and the choice of a suitable contrasting plate, developer and time of development, it is possible to read the length of a line to 0·1 mm.

4. *Photometer Method.*—A convenient instrument for measuring line intensity is the micro-

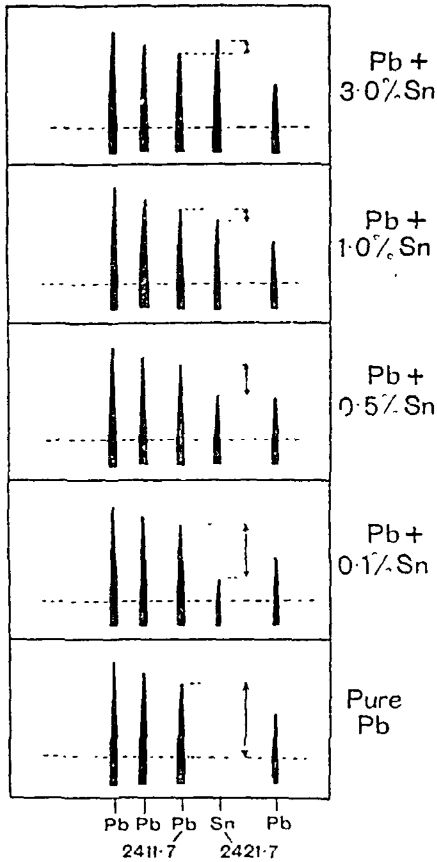

Fig. 3.

photometer consisting of a photo-cell with a fine aperture and a mirror galvanometer, lamp, and scale. The degree of blackening of a line can be determined accurately as a function of the galvanometer deflexion by projecting a spectrum line on to the aperture of the photo-cell. This method eliminates the necessity of proceeding with an analysis in steps, and avoids the difficulty of visual comparison of line intensity.

Applications to Miscellaneous Problems.—The increasing use to which the spectrograph is being put in industrial laboratories indicates that chemists are realising the great advantages which accrue from its use in routine analysis. New methods for increasing its accuracy are frequently being described.

In the study of the coprecipitation of magnesium with calcium as oxalate, Popoff, Waldbauer, and McCann (Ind. Eng. Chem. [Anal.] 1932, 4, 43) used spectroscopic methods. Similarly, Knowles and Martin (Trans. Faraday Soc. 1935, 31, 502) have investigated the precipitation of zinc together with copper as sulphide. Churchill (Ind. Eng. Chem. 1931, 23, 996) has applied the spectrograph to the detection of fluorides occurring in drinking water at a concentration of less than 1 mg. per litre. The extended use of aluminium culinary ware has led to the study of the possible contamination of food by aluminium. Occasionally spectroscopy has been applied to criminology, and a few instances are cited by Judd Lewis (Analyst, 1935, 60, 10). Recently, perhaps the largest field of application has been in the realm of metallurgical analysis (D. M. Smith, "Metallurgical Analysis by the Spectrograph," British Non-Ferrous Metals Research Association, 1933). By these methods the unexpected presence of rare elements has been revealed, e.g. gallium in zinc, germanium in coal ash, scandium in silver. Methods have been described for the analysis of alloys containing up to 10% or more of one element. The quantity of any element capable of detection in a particular case varies with the method of excitation and the nature of the other constituents present. D. M. Smith states that about 5×10^{-5}% of cadmium and 1×10^{-4}% of copper and silver can be detected with certainty in a sample of lead, using an arc method.

Metzger (Ind. Eng Chem. 1935, 27, 112) has shown that 1 part of krypton can be detected in 10^6 parts of oxygen but that 1% of oxygen in krypton cannot be found by spectroscopic means. Spectroscopic analysis has no rival for the rapid detection, and in many cases the quantitative estimation, of impurities in many varieties of material.

Literature.

(In addition to books mentioned in text above, and in SPECTROSCOPY, Dict., Supplement II, 408.)

D. M. Smith, "Bibliography of Literature on Spectrum Analysis," British Non Ferrous Metals Research Association, 1935. A. L. T.

ELECTROCHEMICAL ANALYSIS

Electrical methods of analysis may be considered under three headings, according as they involve (*a*) conductivity measurements, (*b*) deposition of a metal or oxide, or (*c*) measurement of electrode potentials These three sections will be considered in turn.

CONDUCTIVITY METHODS.

The applications of electrical conductivity in analytical work are two-fold : first, for detecting the end-point of a titration, and secondly, for estimating amounts of electrolyte. The conductivity of a solution depends primarily on the concentrations and equivalent conductivities (*i.e.* mobilities) of the ions present, and so it is often possible to detect by appropriate measurement the removal of one kind of ion or its replacement by another. The adaptation of this idea to the determination of the end-point of a neutralisation titration was suggested by Kohlrausch in 1885, but it appears to have been used first by Küster and his co-workers in 1903 : it has since been frequently applied to other reactions, the end-points being generally marked by a change in the direction of the curve representing the conductivity during the course of the titration.

Measurement.—In general, conductivity is measured by means of a Wheatstone bridge arrangement (Fig. 1). The cell C is placed in one arm of the bridge and a known resistance R in the other ; S is the source of $A.C.$, which is used to prevent polarisation at the electrodes, and D is a current detector ; AB is the "bridge-wire," along which can be moved the contact E. When no current is indicated by D the ratio of the resistances (or lengths) of AE to EB is equal to the ratio of the resistances of C to R ; the conductivity of C is the reciprocal of its resistance. The simplest source of $A.C.$ is a small induction coil ; D may then be a telephone earpiece, the sensitivity being increased if required by the use of a thermionic valve

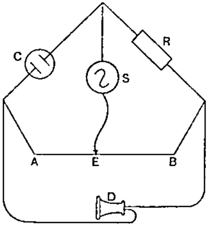

FIG. 1.

amplifier. The noise made by a spark-coil is a disadvantage and moreover it does not give really symmetrical $A.C.$, and so valve-oscillators giving a frequency of about 1,000 cycles are employed. Some workers replace the telephone by an $A.C.$ galvanometer or by a $D.C.$ instrument in conjunction with a dry rectifier of the copper–copper oxide–lead type, the latter arrangement being preferable. Other types of rectifier, *e.g.* valve and crystal, have been employed.

For titration purposes it is not necessary to know the actual conductivity, since any quantity directly related to it is adequate ; this fact is applied in various systems of "visual titration." In one of these the resistance R is kept constant and so also is the position of E, while D is replaced by the primary of a transformer the secondary of which is connected across a dry-rectifier and galvanometer. The reading of the latter can be used, instead of the conductivity of the liquid in C, to determine the end point of a titration. The fixed position of E must be chosen so that the bridge is never actually balanced during the course of the

titration. If high accuracy is not required the *A.C.* electric-light mains, through a transformer, may be used for conductivity work ; a galvanometer is then essential as a detector, since the telephone and ear are insensitive to the 50–60 cycle note. Another simplification for conductometric titration work avoids the use of the Wheatstone-bridge and also employs the *A.C.* mains ; the arrangement is shown in Fig. 2. The bell-transformer *T* steps down the mains voltage to about 3 volts, and the current passes through the cell C ; between the terminals A and B are connected a galvanometer, or millivoltmeter, and a rectifier. The resistance *R*, about 500 ohms, acts as a shunt and is adjusted according to the sensitivity of the meter. The deflection of the latter may be taken as a measure of the conductivity of the solution in the cell C. In some cases A and B have been connected to the grid and filament, respectively, of a thermionic valve, and the variation of the conductivity of C indicated by the reading of a micro-ammeter in the anode circuit. These modifications have made what was at one time a delicate physico-chemical laboratory operation into one suitable for industrial control purposes.

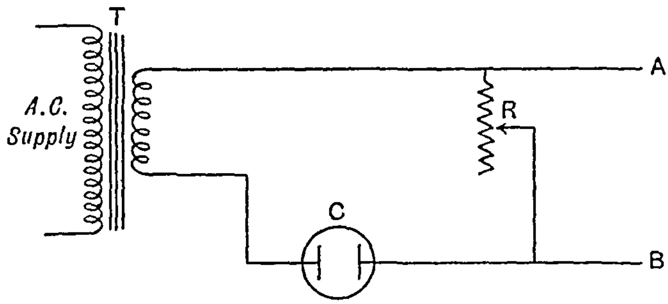

Fig. 2.

Although alternating current is most frequently employed for conductivity work various suggestions have been made for the use of direct current : these are, however, mainly of academic interest. There is available, however, a commercial instrument known as the Dionic Water Tester (Evershed and Vignolles, Ltd.), employing *D.C.* for conductivity determinations, sufficiently accurate for technical estimation of electrolytes and for many titration purposes. It consists of a hand-driven dynamo supplying *D.C.* at 100 volts, which is passed through the solution under investigation ; the current strength, directly proportional to the conductivity, is registered on a suitable meter. The latter is graduated by the makers to read directly the specific conductivity of the solution, an average allowance of 2 volts being made for the polarisation of the gold-plated base metal electrodes.

A variety of cells suitable for conductometric titration have been designed, the essential feature of them all being the provision of means for keeping the two platinum electrodes, generally 1 sq. cm. area, in fixed positions relative to one another ; the ability to stir the titrated solution mechanically is an advantage, and it should also be possible to place the vessel in a thermostat. The electrodes should be platinised in the usual way, by the electrolysis of a platinic chloride solution, but if very highly dilute solutions are being employed, it is perhaps better to avoid the error due to adsorption by the platinum black and use smooth electrodes. In carrying out a titration the conductivity of the solution is measured at the commencement and also after the addition of each of about ten known amounts of titrant ; the end-point, which must be well passed, is determined graphically by plotting the conductivities (or equivalent galvanometer readings) against the volumes of titrant added, as will be seen later. The volume change in the titration should be as small as possible, and this is achieved by using the titrant, in a micro-burette, ten to twenty times as concentrated as the titrated solution. In accurate work a correction for the volume change may be applied. The main advantages of conductivity titration are (*a*) coloured solutions as dilute as 0·0001*N* may be analysed, (*b*) only a limited number of readings is generally necessary, and (*c*) there is no need for special precautions near the end-point, as with other titrations, since it is determined graphically. The chief disadvantages are (*a*) a thermostat is desirable for reasonably accurate work, since the conductivity increases by about 2% per degree, and the solution may well become warm during the titration, and (*b*) the presence of appreciable amounts of foreign electrolytes reduces the accuracy of the results.

Conductometric titrations fall into three main categories : (*a*) neutralisation, (*b*) displacements, and (*c*) precipitation processes. There are one or two cases of oxidation-reduction reactions followed by conductivity measurement, but these are of minor significance.

Neutralisation Titrations.—*Strong Acids and Strong Bases.*—At 18° the equivalent conductivity of the hydrogen ion is 314 and that of the hydroxyl ion is 172, whereas very few other ions have values exceeding 70 reciprocal ohms. In the neutralisation of a strong acid by a strong base the acid is converted into its salt, that is, the hydrion is replaced by the cation of the base, and so the conductivity must decrease. When the acid is completely neutralised the further addition of alkali results in an increase of conductivity, so that the conductivity-titration graph must be as in Fig. 3, I. It can be shown theoretically that the two portions of the graph must be straight lines, intersecting at the equivalence-point, provided there is no appreciable volume change in the titration ; the position of the end-point can thus be found by drawing straight lines through the experimental points (marked with crosses). A strong base when titrated with a strong acid gives a curve similar to Fig. 3, I, since the anion replacing the hydroxyl ion during neutralisation has a lower conductivity.

Very Weak Acids.—When a very weak acid, *e g.* a phenol, dissociation constant 10^{-7} to 10^{-11}, is titrated with a strong alkali the conductivity of the solution increases from the commencement, since the acid is only very slightly ionised and has a low conductivity, whereas the salt formed during neutralisation is a good conductor. When the end-point is passed the conductivity increases more rapidly because the free alkali is a better conductor than the salt, and so a graph of the type of Fig. 3, II, is obtained. On account of hydrolysis the actual conductivity follows the dotted line, but the end-point can still be obtained by finding where the two straight lines cross. The intersection is, however, not very sharp and the results consequently not highly accurate ; in dilute solution the break is even less marked.

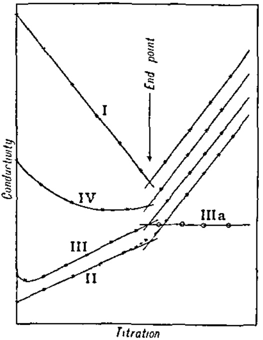

Fig. 3.

Moderately Weak Acids—In the titration of a moderately weak acid, *e.g.* acetic, propionic, etc, dissociation constant 10^{-4} to 10^{-7}, a curve of the type of Fig. 3, III, is obtained ; there is a slight decrease in conductivity at the commencement because of the removal of hydrions, but as the salt accumulates it represses the ionisation of the acid so that it then behaves as if it were a very weak acid (*cf.* Fig 3, II) The sharpness of the intersection can be improved by titration with a weak base, *e g.* ammonia ; the type of curve is as Fig. 3, III*a*. The conductivity of the ammonium salt of the acid is little different from that of the salt of the strong-base, *e g.* sodium, but after the end-point the free ammonium hydroxide contributes very little to the conductivity, which thus remains almost constant.

Moderately Strong Acids.—Acids having dissociation constants between 10^{-2} and 10^{-4}, *e.g.* mandelic and salicylic acids, give conductivity-titration curves of a type intermediate between those of a strong and moderately weak acid, as in Fig. 3, IV : the intersection at the end point is not sharp and so it cannot be determined accurately. To overcome this difficulty ammonia is added, until about one-third of the acid is neutralised, the system is then titrated with a strong alkali ; two sharp breaks are observed, and the amount of strong alkali added when the second of these is reached is equivalent to the total acid originally present. The alkali not only neutralises the remaining acid but also displaces the ammonia from the salt. Alternatively, moderately strong acids may be estimated by reversing the titration and adding the acid to standard alkali in the cell. Whenever alkali is being titrated, however, special precautions must be adopted to prevent access of carbon dioxide from the air.

Mixtures of Acids.—The conductometric method provides one of the best means of estimating a mixture of a strong and a weak acid ; it is then advisable to use a weak base, *e g.* ammonia, as titrant. The conductivity first decreases as the strong acid is neutralised, and when this is complete the curve changes its direction and the conductivity increases ; finally when both acids are neutralised there is a second break and the conductivity remains almost constant.

Applications—Conductometric acid alkali titrations have been applied to various strong acids and bases, to a number of weaker acids, *e g.* amino-acids, boric, carbonic, lactic, mandelic, o-nitrobenzoic, salicylic, succinic, sulphurous and tartaric acids, to a number of phenols, and to various weak bases, *e g* alkaloids, ammonia, aniline, magnesia, methylamines and pyridine. On the more technical side the conductivity method has been used for the determination of carbon dioxide in water, of the acidity of beer, wine, leather tanning liquors and soil extracts, and of the alkalinity of paper digestion liquors. The acid numbers of fatty acids, in alcohol solution, have also been determined by conductometric titration. The principle of estimating a mixture of a strong and a weak acid has been applied to detect the presence of mineral acid in vinegar, and analogous applications are the analysis of mixtures of caustic alkali and ammonia, and of a hydroxide or bicarbonate and carbonate.

Displacement Titrations.—The salt of a weak acid, or of a weak base, may be titrated conductometrically by means of a strong acid, or base, respectively ; the first effect is to produce little change in the conductivity For example, in the titration of sodium acetate by hydrochloric acid the resulting sodium chloride has a conductivity only little greater than that of the acetate removed, and the acetic acid formed contributes a negligible amount. At the end point, however, free hydrochloric acid is present in the solution and the conductivity rises rapidly on its further addition. The intersection of an almost horizontal line, on the conductivity-titration graph, with a rapidly rising one gives the end point.

The principle described has been employed in the estimation of acetates, alkaloids (in the form of salts), ammonium salts, benzoates, carbonates,

phosphates and succinates. The titration of a mixture of a hydroxide and carbonate involves first a neutralisation and then a displacement reaction, two breaks being observed.

Precipitation Titrations.—In the addition of sodium chloride to silver nitrate, for example, insoluble silver chloride is precipitated and the silver ions in solution are replaced by sodium ions having a similar conductivity; the conducting power of the solution thus alters little. After the end-point the further addition of sodium chloride causes the conductivity to increase, since no silver nitrate remains with which it can react. If the conductivity of the ion in the titrant, *i.e.* sodium in the example given, is smaller than that of the precipitated ion, *i.e.* silver, the conductivity will actually decrease whilst precipitation is occurring; the intersection at the end-point will then be sharper than would otherwise be the case. The sharpness can be further increased if the precipitating ion, *i.e.* chloride, has a high conductivity. Errors in conductometric precipitation-titrations may be due to (*a*) the solubility of the precipitate, (*b*) its rate of formation, or (*c*) its uncertain composition. The first two sources of error can frequently be overcome by the addition of alcohol, and the last by titrating a hot solution.

Applications.—Examples of precipitation titrations which have been carried out conductometrically are the following, the titrant being given in parenthesis after the name of the substance being estimated: barium (lithium sulphate); bromide (silver nitrate, mercuric perchlorate); cadmium (sodium sulphide, potassium ferricyanide); calcium (lithium or potassium oxalate, lithium sulphate); carbonate (barium chloride); chloride (silver nitrate); chromate (barium chloride, silver nitrate); cobalt (potassium ferricyanide); copper (potassium ferricyanide); cyanate (silver nitrate); cyanide (silver nitrate); ferrocyanide (silver nitrate, zinc chloride); ferrous ions (sodium sulphide); iodide (silver nitrate or acetate); lead (sodium sulphide, lithium chromate or sulphate, potassium ferrocyanide); potassium in concentrated solution (sodium perchlorate); molybdate (lead acetate); strontium (lithium chromate or oxalate); sulphate (barium acetate, chloride, hydroxide or nitrate); thiocyanate (silver nitrate); thallium (sodium chromate); tungstate (lead nitrate); and zinc, other than sulphate (sodium hydroxide). Nitrating acid, consisting of a mixture of nitric and sulphuric acids, has been analysed conductometrically: the total acid is determined by alkali, and the sulphate in the neutralised solution is titrated by lead nitrate in the presence of alcohol.

Other Applications.—Conductivity measurements have been applied to analytical purposes other than those involving titrations. In any process where there is likely to be a change in the amount of electrolyte, which is either in solution or can be extracted by water, the conductivity method may be used to indicate such a change. The method has the disadvantage that it is unable to distinguish between one electrolyte and another, but for purposes of industrial control, where the same substances always occur, this is not serious. The apparatus, which may be of the Dionic Water Tester type (*v.* p. 693) can then be standardised for the particular conditions under which it is to function. Mains-operated conductivity apparatus can be readily adapted for the purposes of automatic control of industrial processes.

Conductivity methods have been used in connection with the following purposes: the detection of leakage of cooling water, particularly if sea-water, into a steam condenser, and of "priming" of a boiler, both of which result in an increase of conductivity of the condensate, the determination of the amount of dissolved electrolyte in boiler-feed water, and in mineral and potable waters. The estimation of the mineral ("ash") content of sugar and sugar-syrups, of the acidity of water used in retting fibres, of the amount of alkali carried over by mercerised yarn, and of soluble salts in soil, can all be carried out by conductivity measurements. These have also been used to control the composition of the absorbing solution in the manufacture of sulphuric acid.

Bibliography. — Kolthoff, "Konduktometrische Titrationen," 1934; Jander and Pfundt, "Leitfähigkeitstitrationen und Leitfähigkeits-messungen," 1934; Davies, "The Conductivity of Solutions," 1933; Britton, "Conductometric Analysis," 1934; Böttger (editor), "Physikalische Methoden der analytischen Chemie," Leipzig, 1936.

Deposition Methods (Electroanalysis).

In general, the passage of an electric current through an electrolyte results in the deposition on the cathode of any metal, unless it is highly electropositive; if the deposition can be made virtually complete, and the separation of one metal from another is possible, there is at once available the basis of a direct method of analysis. The possibility of employing electricity in analytical work was first suggested by Cruickshank in 1801, but the early applications were for qualitative purposes only. The first use of the electric current for quantitative estimations was made by Wolcott Gibbs (1864) and by Luckow (1865), and this marked the beginning of a highly important aspect of analytical work which has since developed very considerably. Before describing the practical methods of "electroanalysis" the theoretical principles involved will be reviewed briefly.

Deposition Potentials.—When a metal is inserted in a solution of its own ions, *e.g.* silver in silver nitrate solution, a difference of potential (π) is set up between the metal and the solution, given by the equation $\pi = \pi_0 + 0{\cdot}0002T/n \log c$, where T is the absolute temperature, n the valency of the ions under consideration and c their ionic concentration; π_0 is a constant, called the "standard potential," for the given metal, which is the potential when the ions are at a concentration of 1 g. ion per litre. At ordinary temperatures, *i.e.* about 17°, the electrode potential may be written $\pi = \pi_0 + 0{\cdot}058/n \log c$, so that it changes by $0{\cdot}058/n$ volts for every ten-fold change in ionic concentration; the more dilute the solution

the more negative is the potential. All aqueous solutions contain hydrogen ions, and hydrogen gas also acquires a definite potential in contact herewith given by $\pi=\pi_0+0.058 \log [H^\cdot]$, the valency ($n$) being unity. The standard potential of the hydrogen electrode, *i.e.* with gas at 1 atm. pressure and a hydrion concentration of 1 g. per litre, is taken as the zero of the so-called "hydrogen scale" of potential. The potentials of other electrodes can be measured and stated on the basis of this scale, and if the ionic concentration (c) is known the standard potential (π_0) of any metal can be determined. Some of the values obtained are given below: they are for 17°, but the temperature variation is small.

Na −2·71	Cd −0·40	Pb −0·12	Cu +0·34
Mn −1·1	Co −0·29	H ±0	Ag +0·80
Zn −0·76	Ni −0·23	Sb +0·1	Hg +0·80
Fe −0·44	Sn −0·14	Bi +0·23	Au +1·36

From these standard potentials it is possible to calculate the static (or equilibrium) value acquired by any of the metals in a solution of its ions at a given concentration.

The importance of these results is that in order to deposit a metal electrolytically from a solution of its salts, by application of an external source of *E.M.F.*, the potential of the cathode must be made just slightly more negative than the static value (Le Blanc, 1893). If the solution contains several different ionic species, then the metal having the most positive potential in that solution will deposit first; thus from a solution containing simple salts of silver, copper and cadmium, the metals will separate in the order given. From the equation for the electrode potential it can be seen that for the concentration of a particular ion to be reduced to 0·1% of its initial value the cathode potential at 17° must become $3\times0.058/n$ volt more negative than at the commencement; for a univalent metal this is a maximum of approximately 0·18 volt. Provided the static potentials of two metals differ by more than 0·2 volt, therefore, it should be possible, by controlling the cathode potential, to deposit one almost completely, within the limits of experimental error, before the other begins to separate. In a limited number of cases, *e.g.* iron and nickel, the metals deposit simultaneously as a solid solution—separation is then generally not possible under any conditions.

The formation of complex ions frequently changes the order in which metals deposit, because of the different extents to which the simple ions are removed in the complex. If excess of potassium cyanide is added to the solution of silver, copper, and cadmium salts, mentioned above, the order of deposition will now be silver, cadmium, copper. Complex ions play an important part in electroanalysis by permitting the alteration of electrode potentials: thus, the potentials of copper and bismuth in their simple salts are so close that effective separation is impossible, but in the presence of excess cyanide the copper potential becomes so much more negative that bismuth can be separated almost completely before deposition of copper begins.

It is important to remember that the potential of a cathode as measured is determined by the concentration of ions in its immediate vicinity, but this may be quite different from that in the bulk of electrolyte. The potential may thus indicate almost complete removal of a given metal whereas actually an appreciable amount may still remain in solution. The difficulty may be overcome by vigorous agitation, and this is an essential feature of the separation of metals by means of controlled, or "graded," potentials. Stirring has also an important effect in permitting the use of higher current densities (generally abbreviated as *C.D.*, and expressed in amps. per 100 sq. cm.) than is possible with a stationary electrolyte, thus enabling the process to be carried out more rapidly. In normal circumstances the ions to be deposited diffuse from the bulk of the solution to the cathode at a rate equal to their rate of deposition, but as the *C.D.* is increased a point is reached at which the rate of diffusion attains its maximum value, under the operating conditions. This *C.D.* is called the limiting value for 100% efficiency of deposition, and if it is exceeded the cathode potential rises (negatively) until other ions can be discharged to satisfy the requirements of the current. In electroanalysis this must be avoided unless the second ions are hydrogen ions, but even the co-liberation of hydrogen is often inadvisable for other reasons. The use of the controlled-electrode method of separating metals obviates the danger of the *C.D.* exceeding the limiting value, because it is always adjusted (*v. infra*) to prevent a change of potential. For rapid electrolysis, however, it is desirable to use as large a current as possible and so the conditions should be arranged to give a high limiting *C.D.*, at least at the beginning. This may be done by the use of vigorous stirring, or of hot solutions, or both. In a stationary electrolyte the limiting *C.D.* is about 2·7 amp./dm.^{2} for a N-solution at 17°, and is approximately proportional to the concentration; at 70° this is increased 4–5-fold, and an increase of the same order results if the solution is agitated by a stirrer at about 400 revs. per min. It is easily possible, therefore, in an ordinary electrolyte, for the limiting *C.D.* to exceed 10 amps. at the commencement of electrolysis, but as it proceeds and the ionic concentration falls the limiting *C.D.* falls correspondingly; hence the necessity for reducing the current in the controlled-potential method. The more vigorous the agitation the less the need for current reduction and the more rapid will be the electrolysis.

Overvoltage.—There is always a possibility that hydrogen will be evolved in the electrolysis of any aqueous solution: theoretically, this should occur from a N-acid solution at a potential of about ±0 volt and at about −0·8 volt from a N-alkaline solution. Actually, an excess potential, known as "overvoltage," must nearly always be applied to a cathode before hydrogen evolution can begin; the value of the overvoltage varies with the nature of the metal, and some of these values, important for electroanalysis, are quoted below:

Hg 0·78; Zn 0·70; Cd 0·48;
Ni 0·21; Fe 0·2

Overvoltage must be taken into account when considering the possibility of hydrogen evolution during the deposition of a metal. Zinc, for example, should deposit from a N-sulphate solution at about $-0{\cdot}78$ volt; if the solution contains N-acid hydrogen evolution should occur at ± 0 volt, and so no zinc deposition should, theoretically, take place. In actual practice, however, it does, since the overvoltage of hydrogen at a zinc cathode is 0·70, so that zinc and hydrogen are liberated simultaneously. By the use of a less acid solution, *e.g.* acetic acid, the hydrogen evolution potential is made still more negative and quantitative deposition of zinc can occur. Alkaline, especially ammoniacal solutions, are often employed in order to inhibit hydrogen evolution. It may be noted that overvoltage is almost independent of hydrogen-ion concentration, increases with increasing *C.D.*, and generally decreases about 0·02 volt for every 10° rise of temperature.

Although most metals deposit reversibly, that is to say, they begin to deposit when the static potential is just exceeded, the metals iron, cobalt and nickel are exceptional; there is in these instances a deposition overvoltage, which is about 0·2, 0·25, and 0·3 volt, respectively, at ordinary temperatures, but at 90° the values are reduced almost to zero. The marked change in the deposition potential of nickel as the temperature is raised makes separation from zinc possible at 90°, although under ordinary conditions simultaneous deposition occurs; the process is best carried out in ammoniacal solution.

Form of Deposit.—For electroanalytical work it is desirable that the metal should be deposited in a smooth and adherent form; large crystals are liable to drop off and spongy deposits may contain impurities. The nature of the deposit is affected mainly by *C.D.*, concentration and nature of the electrolyte, and temperature. At high *C.D.* the metal is generally fine-grained and smooth, but if the limiting *C.D.* is exceeded and hydrogen is evolved the deposit may become spongy and basic salts and hydroxides may be occluded. Firm, adherent deposits are generally obtained from concentrated solutions and stirring definitely helps in this respect. It is true that the solution must become dilute at the end of the electrolysis, but the proportion of metal then deposited is small, and in any case there is a tendency for the nature of the early deposit to be continued. Increase of temperature generally improves the deposit, although in some cases very hot solutions tend to give poor deposits, especially if the hydrogen overvoltage is reduced to such an extent that gas evolution occurs. It is evident that, as a rule, the conditions for rapid electrolysis are also those for obtaining a satisfactory form of the deposited metal. The nature of the electrolyte is often of importance: complex ions frequently give better deposits than do simple ions, but they may contain adsorbed impurities. The difficulty of obtaining a satisfactory deposit is sometimes obviated by the use of a mercury cathode in which the metal dissolves (*v. infra*).

Apparatus.—*Electrodes.*—The most popular electrode material, for both anode and cathode, is platinum, or better platinum-iridium, as it is stronger. Classen recommended a basin, 9 cm. diam., as cathode with a flat spiral anode, but this is little used at present; it is costly and the electrolyte cannot be easily stirred without loss. For stationary electrolysis a platinum-gauze cylinder as cathode and a spiral of wire inside it to act as anode are satisfactory; so also is the combination of "flag" cathode of gauze, devised by F. Mollwo Perkin, and the "fork" anode of bent wire which is placed symmetrically about it. When the electrolyte is to be agitated the best arrangement probably consists of two concentric gauze cylinders (Sand, 1907; *see also* Analyst, 1929, 54, 275); these electrodes are obtainable commercially. The inner generally acts as anode: it is attached through a steel chuck and rubber tubing to a pulley shaft so

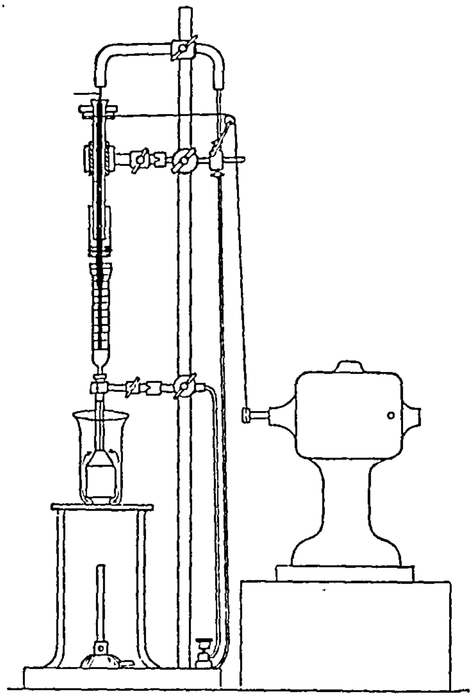

FIG. 4.

that it can be rotated. Electrical connection is made through mercury contained in the rubber tube. The cathode is separated from the anode by a glass tube surrounding the stem of the latter, and the electrical circuit is completed through the clamp holding the stem of the cathode. The whole arrangement is shown in Fig. 4; a speed of rotation of about 500 revs. per min. gives very efficient circulation. Fischer (1907) has used two fixed concentric gauze cylinders, separated by glass strips, and has stirred the solution by a separate paddle of special design; F. M. Perkin, on the other hand, employed a cylindrical gauze cathode which could be rotated, and surrounded it by an anode of two circles of platinum wire fixed one above the other by four small vertical strips, so as to form a cylindrical framework.

The use of a mercury cathode was proposed

by Wolcott Gibbs (1880), but the first successful application was made by E. F. Smith (1903), and was subsequently employed by him and his collaborators. A small quantity of pure mercury at the bottom of a beaker, into which is sealed a platinum wire to make electrical contact, acts as the electrode, and the electrolyte is agitated either by a separate stirrer or by means of a rotating, horizontal perforated disc. The mercury cathode has many advantages; difficulties in the form of the deposited metal do not arise, and hydrogen may be evolved freely without detriment; high *C.D.* may consequently be employed and mechanical stirring may be replaced by the agitation produced by gas bubbles. There is, however, some danger of mercury being carried away by the gas; this can be obviated by attaching a bent tube to the electrolysis cell to act as an air condenser. Base metals, *e g.* zinc, are readily deposited in mercury even from acid solutions, because of the high overvoltage and of the reduced deposition potential associated with amalgam formation. The chief disadvantages of the mercury cathode are its weight, compared with the weight of deposit, the difficulty of drying without loss, and the serious error resulting from the escape of even a minute globule. If the electrolyte contains alkali metal ions these may be deposited in the cathode to form amalgams, but they readily decompose if the solution is acid, and no appreciable error then results. The mercury cathode should not be used for ammoniacal solutions containing ammonium salts, because of the effect of amalgam formation; even nitric acid and nitrates, which reduce to ammonium salts, sometimes cause errors. Although the use of mercury did not attract much notice, except from E. F. Smith and his associates, some attention has been paid to it more recently, and electrodes involving small quantities (10 g) of mercury have been devised (Moldenhauer, Z. angew. Chem. 1929, 42, 331; Tutundžić, Z. anorg. Chem. 1931, 202, 297) Reference will be made later to a special form of mercury cathode for the estimation of alkali metals (*q.v.*).

Many of the advantages of mercury, without the disadvantages, are to be found in the use of Wood's metal as cathode (Paweck *et al.*, Z anal. Chem. 1927, 72, 225; 1929, 79, 115); as it melts at about 70°, it is liquid in the electrolysis of a hot solution. It is actually handled in the cold as a solid, it has a much lower density than mercury, and is not so volatile. Wood's metal may well find many applications in electro-analysis.

The use of amalgamated brass gauze cathodes, proposed by Paweck in 1898, has recently been revived (Paweck and Walther, *ibid.* 1924, 64, 89; Bottger *et al.*, *ibid.* 1933, 93, 401); the cylinder of brass gauze is first cleaned to free the surface from grease and oxides, and then etched in warm dilute sulphuric acid. It is coated with mercury by use as cathode in a solution of mercurous nitrate containing a little nitric acid at a *C.D.* of about 0 3 amp.; it is then washed in water and dipped in hot dilute hydrochloric acid to obtain a bright mercury surface. Some workers deposit as much as 10 g., of mercury, but this is unnecessary; a smaller quantity is sufficient to alloy with the deposited metal without risk of loss being incurred. Precautions must be taken when drying the amalgamated cathode to avoid heating and thus vaporising the mercury.

Tantalum has been suggested as a cathode material instead of platinum, and cathodes of copper and silver gauze have been used for the deposition of the respective metals, as well as in solutions which do not attack them. Reference will be made later to special cases under the headings of the various metals.

Electrode Vessels.—The simplest form of vessel consists of a beaker which should be as small as convenient; the larger the bulk of solution the more difficult it is to deposit the last traces of a metal. Vessels with taps, similar to separating funnels with the tops cut off, have been employed, so that the electrolyte can be run off immediately electrolysis is completed; they suffer from the disadvantages that the liquid just above the tap does not readily mix with the bulk, and also that they cannot easily be heated. Special beakers with siphon-tubes sealed in near the bottom have been employed by some workers, but a loose siphon is probably often quite satisfactory.

Experimental Procedure.—In the following description it will be assumed that the method of graded, or controlled, potentials is used, but this is not always necessary and the resulting simplifications are then obvious. The importance of adjusting the applied *E.M.F.* in the electrolytic separation of metals was first realised by Kiliani (1883), and in 1893 Freudenberg separated metals from one another by controlling the *E.M.F.* of the battery, thus assuming the anode potential to remain constant. A great improvement was made by Sand (J.C.S. 1907, 91, 373) who introduced an auxiliary standard electrode so that the potential of the cathode could be accurately controlled.

The particular anode and cathode (cleaned from grease) to be used are set up in an appropriate vessel, together with arrangements for stirring and heating, if required (Fig. 4); the electrodes are then connected to the source of current, through an ammeter, and an adjustable resistance, capable of carrying 10–15 amp. The tip of the siphon-tube of the reference electrode which is to be used for measurement of the cathode potential, is inserted in the solution to be electrolysed close to the surface of the cathode. The latter and the reference electrode are then connected to an instrument for measuring *E.M.F.*, generally a potentiometer-voltmeter arrangement, as in Fig. 8, p. 708 (*see also* Sand, Analyst, 1934, 59, 328). The nature of the reference electrode is usually not of great importance, as long as it maintains a constant potential; the special vessels at one time in general use, and still frequently illustrated in text-books and catalogues, are no longer considered necessary. A calomel electrode (*see* Fig. 7, p. 703) may be used, or alternatively one containing mercury, mercurous sulphate and sulphuric acid or a sulphate; quinhydrone electrodes, consisting of an acid solution containing a little quinhydrone into which dips a clean platinum wire, are also

recommended. In order to minimise diffusion of the electrolysed solution into the reference electrode the tip of the latter is generally made of narrow bore tubing bent round several times to form two or three loops. In a rapid electrolysis the loss by diffusion can be shown to be negligible, but if desirable the liquid in the tip of the standard electrode may be permitted finally to siphon over into the electrolysed solution.

The electrolysing current is switched on and increased to the value to be employed, generally 1–10 amp., depending on whether ordinary or rapid methods are being used; the cathode potential is then measured. During electrolysis the potential tends to rise (negatively), and the current is decreased from time to time to keep it constant. When the current has fallen to a low value, *e.g.* 0·2 amp. or less, the applied *E.M.F.* is increased so that the cathode potential may become 0·2 volt more negative than the initial value. In this way the concentration of the metal can be reduced to less than 0·1% of its original value, provided the solution is well agitated; no other metal is deposited, provided its potential is more than 0·2 volt more negative than that of the first. The time allowed for the electrolysis is generally half as long again as it takes the potential to attain its final value, but it is always advisable to test the electrolyte chemically for the ions being deposited before stopping the electrolysis. If the metal can be distinguished from the platinum electrode in appearance the depletion of the electrolyte may be tested for by adding water, so that a clean portion of the electrode is covered by the solution; if deposition is complete it will remain unaffected.

The procedure adopted to stop the electrolysis depends on the type of vessel used and on whether the remaining solution is required for further investigation. In the latter case the liquid may be run off by a siphon or the beaker may be removed, and the electrode rinsed with the minimum of water which is added to the bulk of solution. If this is not required water may be added continuously, the excess being siphoned off, or allowed to overflow, until the current drops to zero. Owing to the possibility of re-solution of the deposit on the cathode the current should not be switched off before the electrolyte has been removed completely. The electrode is finally washed well with water, then with acetone, dried in a steam-oven and weighed. Alcohol and ether, at one time widely used for drying purposes, are not recommended, since the peroxide, often present in other, is liable to oxidise the metal. A mercury cathode can be treated in an analogous manner, but it should not be warmed; the acetone may be removed by a current of dry air.

If a second metal is to be deposited from the solution the process is repeated with a fresh, or cleaned, cathode. When the deposition potential of the second metal differs by a large amount from that of the first, or if one metal only is present in the electrolyte, the careful control of potential described above is not necessary. In many instances, however, the evolution of hydrogen can occur, and this may be prevented by controlling the cathode potential. When many separations of the same kind are carried out, or where the potentials of the two metals are reasonably far apart, a "safe" *E.M.F.*, determined by experiment or calculation, may be tapped off and the electrolysis left to itself.

Micro-Methods.—The electroanalytical procedure is readily adapted to the estimation of small quantities of metals; for further details, *see* Pregl, "Quantitative Organic Micro-Analysis"; Lindsey and Sand, Analyst, 1935, 60, 739.

Inner Electrolysis.—The principle of "inner electrolysis," which requires no external current, has been revived in recent years by Sand and his collaborators (*ibid.* 1930, 55, 309, 313, 495, 680). A platinum gauze cylinder acts as cathode, and the two anodes, made of an electropositive metal, *e.g.* zinc or lead, are placed symmetrically on either side of the cathode and enclosed in parchment bags; agitation of the electrolyte is achieved by means of an independent stirrer. The solution to be electrolysed is used as catholyte and a salt of the anode metal acts as anolyte. When anode and cathode are connected externally a small current flows and deposition occurs on the cathode. The method of inner electrolysis has been used to determine small quantities of bismuth in lead (using lead anodes), and small amounts of cadmium and copper in zinc ores, etc. (with zinc anodes).

Applications.—Electroanalysis has been used for the quantitative estimation of a number of metals, to be considered briefly. In addition to cases involving direct cathodic deposition mention will also be made of indirect methods, *e.g.* for alkali metals and for certain anions, of the deposition of oxides on the anode, *e.g.* lead, manganese and thallium, and of instances involving electrolytic processes, *e.g.* reduction of arsenic to arsine, and of nitrate to ammonia, without actual deposition.

Alkali Metals.—Hildebrand's method (1907) involves a principle similar to that of the Castner-Kellner cell for manufacture of sodium hydroxide. An open-ended shallow cylinder, rests on a glass-rod triangle, in a wider flat-bottom crystallising dish, and enough mercury is poured in so as to be about 3 mm. above the bottom of the inner cylinder; thus two separate compartments result. A platinum wire dipping in the outer mercury is connected to the negative pole of a battery, and the anode, placed in the inner compartment, consists of two discs of platinum-gauze fixed one above the other, capable of being rotated. The anode is previously coated with 3–4 g. of silver by electrolysis of an argentocyanide solution. The solution to be analysed, which should be in the form of the chloride, or as the salt of any other acid giving an insoluble silver salt, is placed in the anode compartment, whereas the outer annular space contains a dilute solution of sodium chloride. On electrolysis (about 0·5 amp.) alkali metal amalgam is formed and decomposes in the outer compartment to yield free alkali hydroxide; the decomposition is hastened by the use of a ring of nickel wire having three legs dipping in the outer mercury. When electrolysis is complete the entire con-

tents of the cells, inner and outer, are rinsed into a beaker and the alkali titrated with standard acid.

Alkali metals can be separated from magnesium by this method. The alkali hydroxides are formed in the outer space, but the magnesium hydroxide is precipitated in the inner compartment. Calcium, in the presence of magnesium, is precipitated in a similar manner, although when alone it can be estimated as an alkali metal; barium and strontium also behave like alkali metals, and can be separated from calcium, if magnesium is added.

Anions.—The Hildebrand cell can be used for the estimation of any anion yielding an insoluble silver compound; the latter is deposited on the silvered-gauze anode, which can be washed and weighed. Sulphates may also be analysed by titrating with alkali the liquid in the inner compartment, which contains an equivalent amount of sulphuric acid; a platinum anode should be used.

Nitrates can be reduced to ammonia by electrolysis with a copper cathode in a solution containing a little sulphuric acid and some copper sulphate. The ammonia is distilled off and estimated in the usual manner.

Antimony.—This metal can be deposited from fairly concentrated sulphuric or hydrochloric acid solutions at temperatures of 100° or 50°–75°, respectively. The electrolyte should contain 1–2 g. of hydroxylamine or hydrazine salt, per 100 c.c., and the cathode potential should be controlled. It is advisable to coat the platinum cathode with copper before electrolysis to avoid its being spoilt by the antimony.

The deposition of antimony from thioantimonate solutions is not recommended, because of co-deposition of sulphur; this can be partly avoided by means of potassium cyanide. The antimony solution is made alkaline and a saturated solution of sodium sulphide added, and then 2–3 g. potassium cyanide per 100 ml. Electrolysis is carried out below 65° with a current of 1·2 amps. Antimony may also be obtained quantitatively from neutral tartrate solutions, a temperature of 70°–80°, and a *C.D.* of 0 25–0·55 being employed.

Arsenic.—The quantitative deposition of arsenic is not possible, but small amounts may be estimated by electrolytic forms of the Marsh test. The arsenic is reduced to arsine at a lead or, better, mercury cathode in a special cell in which anode and cathode compartments are separated. Callan and Jones (Analyst, 1930, 55, 90) employ a mercury cathode 1·5 sq. in. in area and about $4N$-sulphuric acid as electrolyte; a current of 2 amps. is passed for 15 minutes followed by 4 amps. for 15 minutes. The gases evolved from the cathode are decomposed in the usual manner to give an arsenic mirror, which is compared with standard mirrors.

The Gutzeit method for estimating arsenic has also been adapted for electrolytic reductions (*see* Fink, J. Biol. Chem. 1927, 72, 737; 1928, 76, 19).

Bismuth.—If a platinum cathode is employed bismuth should be deposited from tartaric, acetic or hydrochloric acid solutions; the potential must be controlled or poor deposits will result. In the tartaric acid method sodium tartrate is added to decompose any mineral acid present in solution, and a rapidly rotating cathode is used. Alternatively, sodium hydroxide may be added until a precipitate just forms; it is dissolved in acetic acid and 2 g. boric acid added to 80 ml. electrolyte. A temperature of 70°–80° is employed, at 0 6–0 7 amp, and the solution is stirred vigorously. In hydrochloric acid solutions the experimental method is the same as for antimony in this medium. When a mercury or amalgamated brass cathode is being used then bismuth may be deposited from nitrate solution containing a little free acid.

In the presence of copper, 10 g. of sodium tartrate, 5 ml of 30% sodium hydroxide and enough 10% potassium cyanide solution to decolorise must be added; bismuth can then be deposited free from copper, the controlled potential method being adopted.

Cadmium.—A variety of methods have been proposed for the electrodeposition of cadmium; the simplest involves the complex cyanide. The solution is made slightly alkaline and then potassium cyanide added until the precipitate first formed redissolves; an excess equal to about half that previously added is then run in. Electrolysis with an initial current of 5–8 amp., using a rotating electrode, may be carried out at 50°. With cyanide solutions there is some danger that the platinum anode will dissolve, this electrode should consequently be small. If copper is present it does not interfere with the deposition of cadmium from the complex cyanide solution, provided the potential does not rise.

Cadmium has also been deposited quantitatively from acetic acid and sodium acetate, ammoniacal and complex oxalate solutions. Very acid solutions are generally avoided because of the simultaneous evolution of hydrogen, although slightly acid (sulphuric) solutions have been employed, especially with the amalgamated brass cathode which has a high overvoltage.

Cobalt.—Ammoniacal solutions are generally used for cobalt deposition, but a substance must always be present to reduce the peroxide formed on the anode. One method is to add excess of ammonia, 5 g. ammonium chloride, and 0 3 g. sodium bisulphite to 100 ml. solution; this is electrolysed at a *C.D.* of 4–7 amps. with vigorous stirring. Another procedure employs phosphate solutions: about 2 ml. of 5% phosphoric acid, and then 20–25 ml. of 10% dihydrogen sodium phosphate are added to 70–80 c.c. of the cobalt solution. Electrolysis begins in the cold at 0 2–0 3 amp./dm²., and then the electrolyte is warmed to 50° or 60° and the *C.D.* increased to 1·2 amps. A small amount of hydroxylamine salt can be added to remove any peroxide on the anode.

The mercury cathode has been employed for the deposition of cobalt from mineral acid solutions.

Copper.—In the absence of noble metals copper may be deposited easily from sulphate solutions, containing a little sulphuric acid (about 0 $5N$), at 70°–80° with stirring. Base

metals, *e.g.* cadmium, zinc, nickel and cobalt, may be prevented from separating by the use of controlled potentials. Nitric acid solutions give good deposits, preferably at a temperature of 18°–30°; about 0·1 g. of urea should be added towards the end of the electrolysis to decompose nitrous acid which interferes with copper deposition.

For separation from arsenate or antimonate (after the addition of tartrate), ammoniacal solutions are employed; excess of ammonia and ammonium sulphate are added to the solution and electrolysis carried out at 70°. If iron is present it should be oxidised to the ferric state; the ferric hydroxide does not interfere with the deposition of copper. Ammoniacal solutions are recommended if the copper solution contains chlorides.

Complex cyanides have been employed for copper deposition (*see* Cadmium), but the method is not generally recommended, although it is sometimes useful for separation from other metals.

Chromium.—It is well known that this metal is difficult to deposit, but small amounts have been estimated, from a chromium salt in dilute sulphuric acid, by means of a mercury cathode.

Chromic salts may be estimated by anodic oxidation to chromate, at platinum, in ammonium oxalate solution; the chromate may then be determined either volumetrically or gravimetrically. The method is applicable to solutions containing iron: the latter is deposited on the cathode.

Gold.—Quantitative deposition has been obtained from complex cyanide, sodium sulphide, and ammonium thiocyanate solutions; for rapid electrolysis the first of these, at a temperature of 50°–60° is preferred. The employment of a mercury cathode permits deposition to be made from auric chloride solutions; attack of the mercury by chlorine liberated at the anode is prevented by adding 10–12 c.c. of toluene to react with the chlorine. Gold is best removed from a platinum cathode by dilute potassium cyanide solution containing a small amount of hydrogen peroxide.

Iron.—With a mercury cathode iron can be obtained satisfactorily from its simple-salt solutions, but otherwise the evolution of hydrogen is troublesome. Oxalate and tartrate electrolytes are generally employed with a platinum cathode: about 7 g. of ammonium oxalate is added to 100 ml. of solution and electrolysis performed at 50°–60°. Towards the end of the process some oxalic acid should be added to dissolve ferric hydroxide which may have formed by the solution becoming alkaline. Electrolysis must not be prolonged otherwise carbon may deposit with the iron.

The electrolytic method has been recommended as giving a clean method for reducing ferric iron to the ferrous state prior to titration by permanganate or dichromate.

Lead.—The cathodic deposits of lead are generally unsatisfactory, this metal is therefore almost invariably estimated by deposition as lead dioxide on the anode; if 5–10% of nitric acid is present no metallic lead separates on the cathode. The addition of 1 or 2% of copper nitrate to the solution is generally advised, as this removes all danger of the deposition of metallic lead. Electrolysis is begun at a low *C.D.* and increased to 2 amps. at ordinary temperatures, or up to 10 amps. with a hot solution and a rotating cathode. When deposition is complete the anode is washed and heated in an air-bath at 220° for an hour. Owing to the remarkable tendency for lead dioxide to retain water the final composition does not correspond exactly to PbO_2, and the factor for conversion into the amount of lead instead of being 0·8662 may be as low as 0·857. The smaller the weight of deposit the closer is the factor to the theoretical value, and an empirical value is generally used according to the amount of lead present. Some workers have heated the dioxide on the anode to convert it completely to monoxide which is then weighed, but this procedure is not recommended. A better method is to dissolve the dioxide, without drying, in standard oxalic acid and titrate the excess with permanganate. The anodic deposition of lead permits its separation from many metals; chlorides, and compounds of selenium, mercury, phosphorus, and arsenic should, however, not be present.

Lead has been estimated by cathodic deposition from hydrochloric acid solutions, or better from solution in excess of sodium hydroxide on an amalgamated brass cathode.

Manganese.—Like lead, manganese is best deposited as dioxide on the anode; the manganese salt, together with 8–10 g. of ammonium acetate, and 1–2 g. of chrome alum to help the deposit adhere to the anode, is dissolved in 100 ml. of water and electrolysed at about 80°. If the solution is stirred 10 ml. of alcohol may be added to prevent frothing. When deposition is complete the anode is washed and heated strongly to Mn_3O_4 which is weighed.

Mercury.—Many methods have been devised for the estimation of mercury, there being no special difficulty in its deposition; the platinum should, however, always be plated with silver before use with mercury. Solutions containing a little sulphuric or nitric acid may be used at temperatures up to 60°. If mercurous salts are precipitated some persulphate should be added to oxidise them before the electrolysis is completed. Deposition may also take place from cyanide solutions in the cold, from electrolytes containing an excess of ammonia, or from alkaline solutions containing sodium sulphide. There is, of course, no objection to the use of a mercury cathode, but deposition should then be made preferably from acid solutions.

Molybdenum.—From electrolytes containing dilute sulphuric acid, molybdenum is deposited as hydrated sesquioxide on the anode; after washing the oxide is dissolved in dilute nitric acid, evaporated to dryness and heated to expel the acid. The residue of H_2MoO_4 is weighed.

Nickel.—This metal is generally deposited from a solution containing 4–5 g. ammonium sulphate and 30–35 ml. strong ammonia at 50°–60°. To prevent the deposition of zinc, if present, the electrolysis should be carried out at about 90°. If nitrate is present there is a danger of the platinum anode being attacked by ammonium nitrite formed during electrolysis:

an iron wire, made passive by dipping in nitric acid, is then generally used as anode. The nickel deposit on the cathode is likely to be difficult to remove; sulphuric acid solution containing hydrogen peroxide is very useful for this purpose.

The complex oxalate method (*see* Iron) has been used for nickel deposition, but as the metal obtained includes carbon it is not altogether satisfactory. If it is required to separate nickel from chromium, aluminium or manganese the oxalate method is used to give a preliminary separation, the deposit is then dissolved in acid and pure nickel deposited from ammoniacal solution. Copper, if present, separates with the nickel from the oxalate bath, but is readily removed subsequently.

Palladium.—Palladium ammonium chloride, with 30% sulphuric acid, or in ammoniacal solution have been employed.

Platinum.—To obtain the metal in a bright adherent form very low *C D.*'s should be employed, *e g.* 0 01–0 05 amp. at 50°–60°, the electrolyte is chloroplatinic acid containing a small amount of sulphuric acid.

Rhodium —This metal has been deposited for analytical purposes from phosphoric acid solutions and from rhodichloride in dilute sulphuric acid

Silver —Although the most coherent deposits of silver are obtained from cyanide solutions these are not recommended for quantitative work unless it is desirable to prevent the deposition of other metals The most accurate procedure is to employ 80–100 ml of electrolyte to which has been added 1–3 ml nitric acid (sp gr. 1 4)—excess should be removed by evaporation with sulphuric acid—and 3 ml of alcohol *(to prevent formation of peroxide on the anode)*, electrolysis is carried out at 80°–90°, the applied voltage not exceeding 1 4 volts. This method permits separation of silver from copper, lead, arsenic (3- or 5-valent), antimony (with tartaric acid), zinc, nickel, cobalt, and other metals. By the use of high temperature and rapid agitation the silver is deposited in a coherent form

For the separation of silver from arsenic and *antimony an ammoniacal solution is sometimes* employed; 3–5 g of ammonium nitrate and 10–15 ml. of concentrated ammonia are added to 100 ml of solution, the electrolysis being performed at room temperature. The voltage must not rise above 1 4, otherwise spongy deposits may be obtained.

Thallium.—The separation of the metal can best be made with a mercury cathode, but it is advisable to add a known amount of zinc sulphate to the solution before electrolysis, the zinc is deposited with the thallium, and in some way prevents loss of the latter. Alternatively thallium may be estimated by deposition as Tl_2O_3 on the anode; 100 ml. of solution contains 3–6 ml. *N* sulphuric acid and 5–10 ml of acetone, and electrolysis is carried out at low *C.D.* (0 02–0 05 amp) at 50°–55° The deposit is dried at 160°–165° and weighed. Some thallium deposits on the cathode during electrolysis, but this dissolves towards the end The *E.M.F.* should be adjusted so as to prevent oxygen evolution.

Tin.—The deposition of tin is satisfactory from complex oxalate solutions. 100 ml of the latter containing 3 6 g. ammonium oxalate and 3 g. of oxalic acid. A little sulphuric acid is added towards the end of the electrolysis to neutralise any ammonium carbonate formed at the anode which might cause the precipitation of stannic oxide The temperature may be raised to 65° during electrolysis. Some authors recommend the addition of a hydroxylamine salt (2–4 g) to the electrolyte. For separation of tin from antimony a thiostannate electrolyte may be employed. it is made by adding yellow ammonium sulphide to the metal solution until the precipitate dissolves. The deposit is, however, liable to contain some sulphur Hydrochloric acid solutions have been used to deposit tin, some hydroxylamine hydrochloride being present to react with the chlorine; the temperature is raised from 30° to 70° during electrolysis and vigorous stirring is employed.

It is generally recommended that the platinum cathode be first covered with copper, and then with tin from an oxalate bath if a thiostannate solution is to be electrolysed, because of the difficulty of stripping tin from platinum It has been stated, however, that the tin deposit can be easily removed by using the platinum cathode covered with tin as an anode in a dilute sulphuric acid solution

Uranium —The *cathode* deposit consists of a hydrated oxide this is generally obtained from an electrolyte containing sodium acetate, and after washing is converted into U_3O_8 by heating strongly

Zinc —This metal is difficult to deposit in a quantitative manner because of the simultaneous evolution of hydrogen, and alkaline solutions *are often used In the zincate method enough* sodium hydroxide is added to produce a clear solution which is electrolysed whilst hot, although it is recommended that it should be cooled before the cathode is removed Nitrates and ammonium salts if present introduce errors. Good deposits can also be obtained from a neutralised solution to which 4 g sodium acetate and 10 drops of acetic acid are added per 100 ml. *By employing a mercury cathode, when the* liberation of hydrogen is not serious, electrolysis of zinc sulphate, even in the presence of free sulphuric acid, is said to be satisfactory.

If a platinum cathode is to be used it should first be coated with silver or copper; alternatively cathodes of nickel gauze or of amalgamated brass gauze will be found quite satisfactory

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Potentiometric Titration.

The fundamental principle of the potentiometric method is that in the vicinity of the end-point of a titration the concentration of the ions being titrated is changing very rapidly: the

potential of a suitable electrode varies regularly with the ionic concentration (*v. supra*), so that near the end-point the electrode potential will change rapidly as the titrant is added. In general the slope of the curve showing the variation of potential during the titration is greatest at the end-point, or expressed mathematically the end-point occurs when the amount of titrant added is such that $\Delta\pi/\Delta v$ is greatest ; $\Delta\pi$ is the change of potential resulting from the further addition of the small quantity Δv, *e.g.* 0·05 ml., of titrant, after v ml. have been already added (*see* Figs. 5 and 6). By plotting the potential, or better $\Delta\pi/\Delta v$, of an

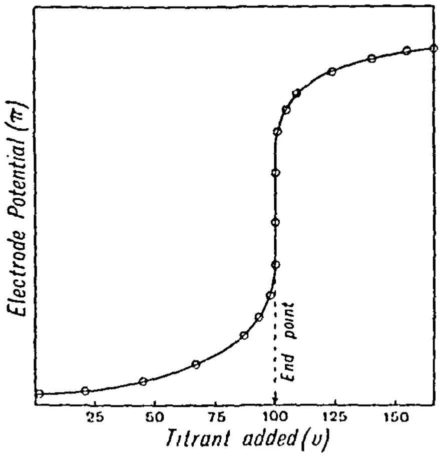

FIG. 5.

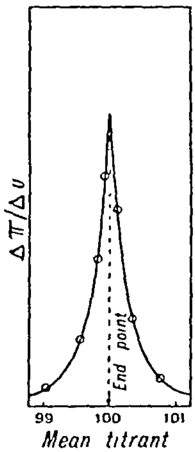

FIG. 6.

appropriate "indicator" electrode, against the volume of titrant, the equivalence-point of a titration can be determined. The potentiometric method can be used with coloured and dilute solutions, when ordinary indicators are of little value, and also for many processes for which indicators are not available. The main disadvantages are the special apparatus required, and the time taken for a titration : since the potentiometric method would normally only be employed when ordinary indicator methods are not possible these disadvantages are not significant.

Measurement of Potential.—The potential of an electrode is measured by combining it with another (reference) electrode of constant potential, so that the two constitute a voltaic cell, the *E.M.F.* of which can be measured. The reference electrode most commonly used is the "calomel electrode," consisting of mercury, mercurous chloride, and a solution of potassium chloride ; this is either 0·1*N*, *N* or saturated, the last being recommended for titration work. Special vessels are often used, and are available commercially, for making up calomel electrodes, but for most purposes a wide-mouthed (2 oz.) bottle will serve (Fig. 7). The ends of the siphon-tube shown are plugged with tight rolls of filter-paper to minimise diffusion, and the tube should be easily removable, so that the potassium chloride solution it contains may be replaced from time to time. If in the solution being titrated a substance is present which is liable to react with potassium chloride, *e.g.* silver ions, it is advisable to use an intermediate vessel between the reference electrode and the titration system ; connection is then made by means of a second siphon-tube containing potassium nitrate or sulphate, or ammonium nitrate solution. Other reference electrodes, *e.g.* mercury-mercurous sulphate-sulphuric acid, or a quinhydrone electrode with potassium chloride and a buffer solution, may be employed if more convenient, but nothing must be introduced which is likely to affect the titration. The *E.M.F.* of the cell consisting of reference and indicator electrodes is measured by applying some form of the Poggendorff principle ; commercial potentiometers are based on this prin-

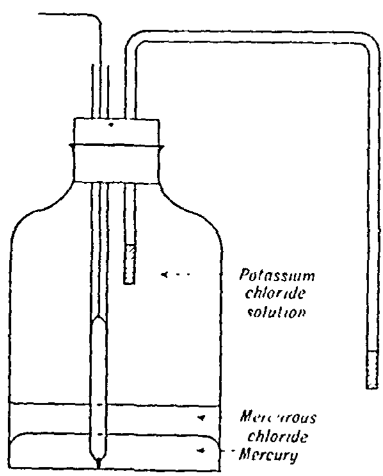

FIG. 7.

ciple, but these, although convenient, are not essential for titration purposes, and the arrangement depicted in Fig. 8 may be adopted. A 2-volt accumulator A is connected across a "metre-bridge," or better a bridge-wire of the spiral type wound on a cylinder (BC) ; the combination of reference electrode (R) and indicator electrode (I), inserted in the solution

to be titrated, is connected between B and the moving contact E. A pointer galvanometer with a sensitivity of 1–2 divisions per micro-amp. is inserted at G and a suitable switch at *S*. The contact E is moved until no flow of current is observed on G when S is closed. The resistance (or length) of the wire BE is directly proportional to the *E.M.F.* of the measured cell. By means of a standard cell of known *E.M.F.* it is possible to calibrate the potentiometer wire BC so as to read off the actual voltage of any other cell, but this is unnecessary for titration purposes. Changes of electrode potential are required to indicate the end-point, and consequently any quantity proportional to the *E.M.F.*, *e.g.* length of the wire BE, will serve the purpose ; for the same reason it is not necessary to know the potential of the reference electrode, since it remains constant.

In the potentiometer-voltmeter modification (Sand, 1907) the uniform wire BC can be conveniently replaced by two variable resistances,

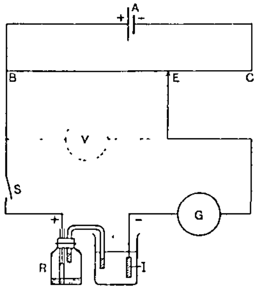

Fig. 8.

such as are used in radio-apparatus, one fine and the other coarse, joined in series. The terminal B is connected to the moving contact of one resistance and E to the other, and their positions adjusted until no current flows through G on closing the switch. The *E.M.F.* of the cell is then indicated directly on the millivoltmeter V inserted in the position shown in Fig. 8 ; a milliammeter or a galvanometer, with a series resistance, may be used as a voltmeter.

Process of Titration.—Special vessels have been devised for carrying out potentiometric titrations conveniently, but these are not essential. The solution to be titrated is placed in a suitable vessel, the appropriate indicator electrode (*v. infra*) inserted and the reference electrode connected. The *E.M.F.* of the cell so formed is measured, and known volumes of titrant added ; after each addition the solution is stirred well, if possible by a mechanical stirrer or by a stream of suitable gas, and the *E.M.F.* is measured again. Near the equivalence-point, the approximate position of which may be determined by a preliminary rough titration, the titrant should be added 0·05–0·10 ml. at a time, and a minute or two allowed for equilibrium to be attained before the potential is measured. The end-point can then be obtained graphically, as already indicated (Figs. 5 and 6).

Special Methods.—*Simple Reference Electrodes.*—A capillary tube containing a platinum wire is placed in the solution to be titrated to act as reference electrode ; a little of the solution is drawn into the capillary, and as it mixes only slowly with the bulk it can be regarded as remaining unchanged throughout a titration. The potential acquired by the platinum is thus approximately constant. For approximate work the end point may be detected by means of a galvanometer and series resistance connected across the two electrodes, no potentiometer being necessary ; the galvanometer shows little deflection until the end-point is approached when a definite swing is observed. An analogous device is to seal a platinum wire into the outlet tube of the burette containing the titrant ; this acts as a constant reference electrode. The tip of the burette must dip into the titrated solution to make contact, and back diffusion is eliminated by bending the outlet tube twice at right angles. This arrangement requires the use of a potentiometer. It is frequently possible to find a pair of electrodes one of which responds to change of a particular ion, whereas the other does not ; the latter can then function as a constant reference electrode, and the *E.M.F.* of the cell made up of the so-called " bimetallic system " dipping in the titrated solution is small until the end-point is reached, when it increases rapidly. A galvanometer is again sufficient to indicate the end of the titration. Examples of bimetallic systems are antimony, as the indicator electrode, together with natural graphite, carborundum, cadmium, nickel or cobalt as reference electrode for neutralisation titrations ; platinum and tungsten are a suitable pair for oxidation-reduction processes.

When many titrations of the same kind are to be performed the solution to be titrated may be connected, by means of a siphon tube filled with neutral electrolyte and having its ends plugged with filter paper,. to another vessel containing a suitable comparison electrode and electrolyte, the potential being equal to the value which the titrated solution should have at the required end point. The comparison electrode may consist of an actual solution previously titrated, or made up to be equivalent to it, or it may be a system of quite different nature giving the same potential. The indicator and comparison electrodes are connected through a tapping key to a galvanometer, and the titration performed. Before the end-point the current flows in one direction, but it is reversed when the end-point is passed; at the actual end-point the *E.M.F.* of the system is zero and no current flows.

Differential Titration.—The principle, first introduced by Cox in 1925, has been widely developed. If to two identical solutions are added v ml. and $v+0\cdot1$ ml. of titrant severally, the difference of potential between two similar

electrodes in the two solutions is a direct measure of $\Delta\pi/\Delta v$, where Δv is 0·1 ml., at the point corresponding to the addition of $v+0{\cdot}05$ ml. of titrant. The difference of potential will thus be a maximum at the end-point of the titration. In the original method the solution to be titrated was divided into two equal parts and titrant added from two separate burettes, but subsequently devices have been employed for preventing temporarily small quantities of the titrated solution, surrounding one of the electrodes, from mixing with the bulk before each addition of titrant. For most purposes the end-point can be determined without a potentiometer, a galvanometer being sufficient to indicate the point at which the difference of potential between the two identical electrodes is a maximum.

A type of differential titration is also possible by the aid of a thermionic-valve voltmeter: the titration system, consisting of indicator and reference electrodes of the normal type, is included in the grid-circuit of the valve, and a galvanometer is placed in the anode-circuit. As the end-point of the titration is approached the grid-bias is adjusted, by the aid of a suitable battery, so as to bring the galvanometer pointer back to zero; the magnitude of the deflection resulting from the addition of a definite amount of titrant, *e.g.* 0·05 ml., is then a direct measure of $\Delta\pi/\Delta v$, and so is a maximum at the end-point.

Applications.—The types of titration which can be carried out potentiometrically are suitably considered under three headings: neutralisation (introduced by Böttger, 1897); precipitation (introduced by Behrend, 1893); and oxidation-reduction (introduced by Crotogino, 1893).

Neutralisation Processes.—When an acid and a base are titrated against one another the hydrogen-ion concentration undergoes change, and so it is necessary to have an electrode the potential of which responds to changes in this ion. Several such electrodes are available, *e.g.* hydrogen gas, oxygen gas (or air), quinhydrone, antimony or glass (*see* "Hydrogen Ion Concentrations"). If accurate results are required the hydrogen-gas or quinhydrone electrodes should be used, provided the solutions to be titrated are such as to permit their employment. The glass electrode is also capable of giving precise results, but the technique is difficult. The quinhydrone system cannot be used in solutions more alkaline than p_H 8, and so it is advisable to add alkali to acid when employing this electrode. For approximate work the air and antimony electrodes may be found convenient.

The accuracy with which the end-point can be found potentiometrically depends on the actual change of potential ($\Delta\pi/\Delta v$) at the equivalence-point. When a strong acid and base are titrated the maximum value of $\Delta\pi/\Delta v$ is large, even in dilute solution, and good results are easily obtained. In the neutralisation of a weak acid by a strong base, or strong acid by a weak base, the change of potential is not large, and further the maximum $\Delta\pi/\Delta v$ does not coincide exactly with the equivalence point. Provided cK is greater than 10^{-8}, however, where c is the concentration of the titrated solution and K the dissociation constant of the weak acid, or weak base, the break in the potential-titration curve is appreciable and the divergence between the true equivalence point and the indicated end-point is well within the limits of experimental error. It is rarely necessary to titrate a weak acid by a weak base, but by careful potentiometric procedure it is possible to estimate the end-point for a $0{\cdot}1N$-solution within about 1%.

The separate acids (or bases) in a mixture can often be titrated potentiometrically, provided there is an appreciable difference in their strengths, *e.g.* acetic and hydrochloric acids. If c_1 and c_2 are the concentrations of two acids (or bases) in a mixture, and K_1 and K_2 their dissociation constants, then provided c_1K_1/c_2K_2 is greater than about 10^5, two separate breaks will be observed in the potential-titration curve if a strong base (or acid) is used as titrant. The first break indicates neutralisation of the stronger acid (or base), and the second complete neutralisation. The value of K for a strong acid or base, for purposes of computation, may be taken as unity. The general relationship may be extended to successive pairs in a mixture of several acids, or bases.

The salt of a weak acid (or base) may be estimated by titration with a strong acid (or base), the conditions for good results being similar to those for the titration of the weak acid (or base) itself by a strong base (or acid).

These generalisations should be sufficient to indicate the conditions under which end-points of titrations involving acids and bases may be determined potentiometrically; it is consequently unnecessary to enumerate any of the very large number of titrations which can be performed.

Precipitation Processes.—When a solution of one ion, *e.g.* $Ag^{\cdot}$, is titrated with that of another, *e.g.* Cl', with which it forms an insoluble salt, the concentration of the former ion decreases during the process, the decrease being relatively most rapid near the equivalence-point. The potential of a silver electrode placed in the titrated solution will evidently change in an analogous manner. If the solutions titrated against one another have the same concentration and the precipitate is formed by two ions of the same valency, *e.g.* AgCl, the maximum value of $\Delta\pi/\Delta v$ occurs exactly at the equivalence-point. When the two ions have different valencies the maximum occurs either before or after the true equivalence-point, according as the valency of the titrant is greater or less than that of the titrated ion. The error is smaller the smaller the solubility of the precipitated compound, the smaller the volume of the solution and the greater the concentration of the titrated ion. In any case, in order for the inflexion in potential near the end-point to be appreciable, the same conditions must apply; it follows, therefore, that when the position of maximum $\Delta\pi/\Delta v$ can be determined with accuracy the titration error due to the different valencies will be negligible.

The most important type of precipitation-titration followed potentiometrically is that

involving silver nitrate as reagent in conjunction with a silver indicator electrode. This is prepared from a clean silver wire or by coating platinum gauze with silver by the electrolysis of an argentocyanide solution; in the latter case the electrode must be washed free from all traces of cyanide. The electrode should be cleaned, preferably by scraping and then with nitric acid, after each titration. The following are examples of the chief titrations with the silver electrode employing silver nitrate; the latter is generally the titrant.

Arsenate and Arsenite.—The solution must be kept at about p_H 9, *i.e.* just pink to phenol phthalein during the titration, sodium hydroxide being added if required. The results are not very accurate.

Chromate.—The titration should be carried out in the presence of 45% alcohol: this decreases the solubility of the precipitate and increases the inflexion at the end-point.

Cyanide.—Two breaks are observed in the potential titration curve: the first corresponds to the formation of $Ag(CN)_2'$ and the second to the precipitation of all the cyanide as AgCN.

The cyanide titration may be used for the indirect estimation of cobalt nickel, and zinc: excess of a standard solution of potassium cyanide is added and back-titrated with silver nitrate to the first inflexion, corresponding to the formation of $Ag(CN)_2'$ from the excess free cyanide. The remainder of the cyanide is then present either as $Co(CN)_6'''$, $Ni(CN)_4''$, or $Zn(CN)_2$, respectively, and thus the amount of the corresponding metal can be determined.

Halides.—Chloride, bromide and iodide ions in solution may be titrated with great accuracy. Even in dilute solutions satisfactory results are obtainable: with chloride at 0·001N, bromide at 0·001N, or iodide at 0·0005N, the error need not be more than 1%. Theoretically, it should be possible to estimate the amounts of the separate halides in a mixture, since the breaks for complete precipitation occur in the order of increasing solubility of the silver salts, *i.e.* first iodide, then bromide and finally chloride. A source of error is the adsorption of one silver halide by another; this is best obviated by addition of 5% barium nitrate to the titrated solution. Ammonium nitrate may be used instead, and this is recommended when detecting small amounts of chloride in the presence of iodide. If it is desired to estimate traces of Cl' in the presence of other halides, it is preferable to destroy the latter, for example, by boiling with sulphuric acid and sufficient permanganate (*see* Clark, J.C.S. 1926, 764).

Mixtures of cyanide with halides can be titrated potentiometrically; the first inflexion is due to the formation of $Ag(CN)_2'$, then follows that for silver iodide. If chloride and bromide are present these precipitate together with silver cyanide, and so the third break corresponds to the complete formation of these silver salts. It is thus not possible to estimate chloride and bromide separately in the presence of cyanide, but one or the other can be determined, since the amount of cyanide can be obtained from the $Ag(CN)_2'$ break. The results are generally accurate to about 1 or 2%.

For the determination of silver itself in solution best results are obtained with sodium or potassium chloride as titrant.

Phosphate.—The method is the same as for arsenate.

Sulphide.—Alkali or hydrogen sulphide can be titrated by silver nitrate with good accuracy: some authors recommend the use of an ammoniacal silver solution as titrant. The sulphide solution should be more concentrated than 0·02N; if more dilute, better results are obtained by titrating with mercuric chloride, using a mercury indicator electrode.

Thiocyanate.—This is best titrated in the presence of 1% barium nitrate to minimise adsorption errors. Silver bromide and thiocyanate have similar solubilities and precipitate together; hence it is not possible to estimate each separately in a mixture. Chloride and iodide, especially if barium nitrate is added, and cyanide can be titrated in the presence of thiocyanate: the first break indicates completion of $Ag(CN)_2'$ formation, the next silver iodide, and the third to the complete precipitation of silver bromide, chloride, cyanide, and thiocyanate. It is evident that limited mixtures only can be analysed potentiometrically, but even then the method is superior to any other.

Oxidation-Reduction Processes.—In the past the potentiometric method has found its main scope in oxidation reduction titrations, but the discovery of suitable indicators has tended to minimise the importance of this application. The titration of a reduced substance, Red. I, by an oxidising agent, Ox. II, may be represented in its simplest form by: Red. I + Ox. II ⇌ Ox. I + Red II, where Ox. I and Red. II are the oxidised and reduced forms, respectively, of I and II. In the vicinity of the end point the concentration of Red. I decreases rapidly, whereas that of Ox. I increases correspondingly. An unattackable electrode, *e.g.* a clean, smooth, platinum wire or foil, placed in the titrated solution attains a potential determined by the ratio of the concentrations (Ox. I)/(Red. I); hence near the equivalence point the electrode potential will undergo rapid change. The maximum $\Delta\pi/\Delta v$ does not coincide exactly with the true end-point, but the discrepancy is very small if the equilibrium constant of the titration process, *i.e.* (Ox. I) (Red. II)/(Red. I) (Ox. II), is large. The more complete the oxidation of Red. I by Ox. II in the titration the smaller will be the error. The inflexion in the potential titration curve near the equivalence point is greater the larger the equilibrium constant and the more concentrated the titrated solution; hence, under such conditions that the reaction in the titration is virtually complete, the end-point can be determined accurately, provided the solutions are not too dilute.

As a general rule an oxidation reduction electrode is set up very simply: a clean platinum wire is inserted into the solution, and equilibrium sets in rapidly after each addition of titrant. In some instances the potential depends on the p_H of the electrolyte, and so care should be taken to avoid changes in the acidity due to extraneous causes. The following

are the chief estimations which can be carried out potentiometrically.

Arsenic.—Tervalent arsenic may be titrated in concentrated hydrochloric acid solution ($4N$ at end of titration) with ceric sulphate, iodine monochloride (made by dissolving 2 mols. potassium iodide, about $0{\cdot}007M$, to 1 mol. iodate in water, and adding an equal volume of concentrated hydrochloric acid) being added as catalyst. In a slightly alkaline solution, for example, in presence of sodium carbonate, arsenite may be titrated very accurately with permanganate. Sodium hypobromite can also be used as titrant in alkaline solution ; $0{\cdot}001N$-arsenite can thus be estimated within 1%. The titration of tervalent arsenic in 5% hydrochloric acid by means of bromate is particularly suitable for dilute solutions.

Antimony.—In the tervalent state antimony may be titrated with dichromate, bromate or ceric sulphate in acid solution : in the latter case $0{\cdot}0005M$-iodine monochloride should be present as catalyst. The antimony should be reduced, if necessary, by means of sulphite and acid before titration. Antimonates may be titrated quantitatively with titanous chloride (or sulphate) at 90°–95° ; arsenates do not interfere.

Aromatic Amines.—The amine is dissolved in 100 ml. of $2N$-hydrochloric acid, 10 ml. of 20% potassium bromide added and the resulting solution titrated with $0{\cdot}2N$-potassium bromate. The inflexion occurs, in general, when the formation of the tribromo-compound is complete.

Azo-Compounds.—Excess of titanous chloride is added in hydrochloric acid solution, the mixture boiled for 5 minutes, air being absent, and then back-titrated with ferric alum, in the presence of thiocyanate, at room temperature. In certain cases direct titration of an azo-compound with a titanous solution can be performed using Rochelle salt as a buffer.

Cerium.—Ceric sulphate can be estimated in a variety of ways, since it is so often used as titrant ; ferrous (ammonium) sulphate and sodium oxalate are, however, probably best (*see* Oxalic Acid).

Copper.—Solutions of copper, even when quite dilute, may be titrated, in the presence of acetic acid, with thiosulphate after the addition of potassium iodide ; nickel, bismuth, aluminium, zinc, silver, lead and stannic tin do not interfere. The harmful effect of ferric iron is eliminated by adding sodium pyrophosphate. Copper solutions to which excess of iodide or thiocyanate have been added may be titrated with titanous solution at 55°. If ferric salts are present these should be reduced first, then potassium thiocyanate added and the copper titration completed in acid solution at room temperature.

Dichromate.—The usual titration with ferrous iron in acid solution can be performed potentiometrically, and in the presence of 20% sulphuric acid dichromate may be estimated by arsenious oxide. The latter method is of particular use in vanadate solution, since in the presence of a little ferric iron this is not reduced by the arsenious oxide. Cobalt and, particularly, manganese interfere with the titration, but nickel, phosphate and molybdate do not.

Ferric Iron.—For the direct titration a titanous salt appears to be best : the ferric solution should be acid and the reaction should be carried out at room temperature. Copper salts do not interfere.

Ferrous Iron.—The end-point for any of the usual titrations, *e.g.* with dichromate, permanganate or ceric solution can be determined potentiometrically if required.

Ferricyanide.—Titanous chloride, or sulphate, can be used for the titration which should be performed at ordinary temperatures. Accurate results are obtainable in tartrate solutions.

Ferrocyanide.—Estimation by permanganate gives accurate results ; the titrated solution should be about $1{\cdot}5N$ in sulphuric acid. It has been stated that hydrochloric acid does not interfere with the process. Ferrocyanide in 1–$2N$-acid solution may be estimated with ceric sulphate.

Hydrogen Peroxide.—The titration with ceric sulphate is relatively slow, and equilibrium is established more rapidly in $0{\cdot}5$–$3N$-hydrochloric or acetic acid solution.

Hydroquinone.—This can be estimated potentiometrically by iodine, but very accurate results, in acid solution, are obtainable with ceric sulphate as titrant ; the results are so exact that the method has been proposed for the standardisation of ceric solutions.

Hypochlorite.—The titration by arsenious oxide should be carried out in bicarbonate solution.

Iodide.—In $0{\cdot}2$–$0{\cdot}5N$-acid, solutions can be accurately titrated with permanganate. This process may be utilised to estimate bromate and iodate : an excess of standard potassium iodide is added and the residue back-titrated with permanganate. The direct titration of iodide by iodate, in the presence of sulphuric acid, can also be carried out accurately ; the method can be used to determine either iodide or iodate.

Lead.—If the solution is more than $0{\cdot}01M$, lead may be estimated by standard ferrocyanide, containing a little ferricyanide to set up a reversible oxidation-reduction system ; the titration is best performed at 75°. Large amounts of acetate interfere with the process because of the formation of complex ions containing lead.

Mercury.—Mercurous mercury is estimated by oxidising with hot (not boiling) ceric sulphate in an acid solution, and back-titrating excess of cerium with standard ferrous solution. The mixture should contain a large excess of cerium, but not too much acid. If appreciable amounts of mercuric compounds are present a blank estimation should be carried out with an approximately equal amount of mercuric salt. In the mercuric form, mercury may be determined by titanous solution ; to 200 ml. of titrated solution should be added 2 g. tartaric acid, 3–10 g. ammonium acetate (depending on the acidity), 15 g. ammonium chloride, and 5–10 ml. $0{\cdot}1N$-bismuth chloride to act as catalyst. The actual titration is carried out in the cold, after boiling to expel air.

Nitrite.—With permanganate as reagent, the nitrite is run slowly into a definite amount of

the acidified solution at 15° ; the process may also be performed with ceric sulphate as oxidising agent.

Nitro-Compounds.—About 30 ml of 20% tri sodium citrate are added to the solution to be titrated, and air removed by carbon dioxide ; titanous solution, standardised against ferric alum in the presence of citrate, is then added slowly until the solution is dark violet. The excess of titanous salt is back titrated with a standard ferric solution.

Organic Acids and Salts.—Citric, glycollic, malic, malonic, and tartaric acids can be oxidised *by heating for 30–60 minutes at 90°–100° with excess ceric sulphate in 2–3N-sulphuric acid.* The results are reproducible but not stoicheio metric, and it is necessary to find the appropriate factor for the ceric solution by separate experiments with each acid under the conditions em ployed in the estimation.

Oxalic Acid and Salts.—This acid differs from those just mentioned in so far as it is oxidised stoicheiometrically to carbon dioxide and water by means of ceric sulphate : the process may be carried out in *N*-hydrochloric or sulphuric acid at 70°–90°, or at room temperature if 0 0005*M* iodine chloride is added. Very ac curate results are obtainable, and sodium oxalate can be used to standardise ceric solutions (*q v*). The method may be employed to estimate metals forming insoluble oxalates , the precipitates can be dissolved in acid and titrated in the manner indicated. The familiar titration of oxalic acid at 70° in the presence of sulphuric acid by means of permanganate can be performed potentiometrically.

Permanganate.—Any of the processes in which permanganate acts as titrant may be applied equally to its estimation ; the best results are probably obtained with ferrous salts, iodides, or oxalic acid.

Phenols.—The method, using bromate, is the same as described for aromatic amines (*q.v.*).

Sulphurous Acid and Salts—An excess of standard permanganate is added to the alkaline sulphite solution which is then acidified ; the remaining permanganate is removed by a small excess of standard iodide, and the latter finally back-titrated with permanganate Alternatively sulphites may be estimated by running into standard iodate containing 1–3*N*-sulphuric acid ; two breaks are observed in the potential-titration curve, the first corresponds to the *formation of sulphate and free iodine, and the* second to sulphate and iodide ions.

Thiosulphate.—The conventional titration with iodine is probably best for potentiometric estimation.

Tin.—Stannous tin may be quantitatively oxidised to the stannic state by permanganate or dichromate. In strongly alkaline solution *stannous ions may be estimated by ferrocyanide* containing a little ferricyanide.

Titanium.—After reduction to the titanous state in a cadmium reductor (Treadwell, Helv. Chim. Acta, 1921, 4, 551) titanium can be titrated in various ways, the employment of permanganate being recommended. In the presence of iron the first break in the potential-titration curve corresponds to the completion of the process $Ti^{III} \rightarrow Ti^{IV}$, and the second to $Fe^{II} \rightarrow Fe^{III}$.

Uranium.—The uranium compound is first reduced in a slightly acid medium to the U^{IV} state in the cadmium reductor (*v. supra*) : the solution is then warmed and titrated with permanganate in a current of carbon dioxide, when the oxidation $U^{IV} \rightarrow U^{VI}$ takes place. If ferrous iron is present it is subsequently oxidised and a second break is observed in the titration curve. The reduction of U^{VI} to U^{III} may be carried out quantitatively with a titanous salt in a solution containing a large amount of *Rochelle salt at 75°. If a ferric salt is present it may be first estimated in hydrochloric acid* by the titanous compound ; Rochelle salt is then added and the uranium determined.

Vanadium.—Vanadyl solutions can be titrated in fairly concentrated acid solution with either permanganate at ordinary temperatures or ceric sulphate at 50°–60° ; in the presence of ferrous iron the first break in the potential, in either case, represents its complete oxidation to the ferric state, and the second the oxidation of the vanadyl (V^{IV}) to the vanadate (V^{V}) state. The ceric titration has been adapted to the estimation of vanadium in steel (Willard and Young, Ind. Eng Chem. 1928, 20, 972). Vanadyl ions can also be oxidised to vanadate in an alkaline medium by ferricyanide , if caustic alkali is present the reaction is rapid at room temperatures Air should be excluded during the titration and a current of nitrogen, free from oxygen, bubbled through the solution. The reverse process, reduction of vanadate to vanadyl ions, in acid solution may be performed quantitatively by ferrous sulphate, and the end point determined potentiometrically. This reaction has also been used to estimate vanadium in steel (*Idem, ibid.* 1928, 20, 764, 769).

Zinc.—The titration of zinc in neutral solution with ferrocyanide, containing a little ferri cyanide, may be followed potentiometrically, the break occurring when all the zinc is precipitate as $K_2Zn_3[Fe(CN)_6]_2$. As the electrode attains equilibrium slowly, the titration is performed at 65°, even then the results are about 1% low. The addition of 20 g ammonium sulphate to 100 ml. solution decreases the error if the titration is carried out at room temperature, but the process is very slow. Ferric iron (or ferrous iron after oxidation) may be prevented from interfering by adding ammonium fluoride *to a slightly acid solution*; zinc may thus be titrated in the presence of iron. If lead is present the titration should be continued until both metals are completely precipitated ; the titration is then repeated after the addition of a slight excess of sulphuric acid to precipitate the lead, so that the amount of zinc is thus obtained. A better method for the estimation of zinc is to *add excess of ferrocyanide and then* sufficient sulphuric acid to make a *N*-solution ; the residual ferrocyanide is then titrated with permanganate and the end-point obtained potentiometrically.

Bibliography.—Kolthoff and Furman, "Potentiometric Titrations" ; Müller, "Die Elektrometrische Massanalyse" ; Sutton, "Volumetric Analysis," 1935, p 143.

S. G.

PHYSICAL METHODS IN CHEMICAL ANALYSIS.

Spectrographic Analysis.—*See* section "ANALYTICAL APPLICATIONS OF SPECTROSCOPY," p. 688–692.

Absorption Spectra.—*Methods for Mapping Ultra-violet and Visible Absorption Spectra.*—Recently the use of various simplified forms of hydrogen lamp giving continuous ultra-violet radiation has become common, following a realisation of the advantages of this type of spectrum over line spectra for absorption work. The microphotometer also shows to advantage with absorption spectra obtained with the hydrogen lamp, and by its use efforts have been made to derive all the absorption data normally required from the spectrum photograph directly. In the method of Moll, Burger, and Reichert (J. Sci. Instr. 1935, 12, 148) the absorption spectrum of a solution and six comparison spectra for the solvent are obtained with a single exposure. The intensities of the comparison spectra are graduated in a known manner, so that at any given wave-length the intensity of the absorption spectrum can be measured by interpolation between two comparison spectra. This procedure is somewhat protracted and is obviated in the method of Gull and Martin (J. Sci. Instr. 1935, 12, 379) in which one exposure is given for the solution and is followed by a number of exposures for the solvent, starting with that given for the solution and then decreasing by amounts calculated to give a suitable range of extinction coefficients. The absorption spectrum together with the other spectra are recorded with a microphotometer in such a way that the absorption curve is traversed by a series of lines corresponding to known extinction coefficients. It is then possible to read directly from the record the extinction coefficient appropriate to any point on the absorption curve. A similar technique is available in the visible spectrum using a tungsten filament lamp in place of the hydrogen source.

Dielectric Constant.—The dielectric constant of a substance is defined as the ratio of the capacity of a condenser when its plates are immersed in the substance to its capacity *in vacuo.* This ratio is denoted by ϵ and is constant over a wide range of frequencies. Measurements can be made under static electrical conditions corresponding to infinite wave-length, or at any frequency up to 10^9 cycles per sec. At frequencies above 10^7 the technique is rather difficult and the results liable to large errors. Measurements under static conditions are not much used and the bulk of work is carried out with a frequency of 10^5–10^6 cycles per second. Such a frequency has the advantages that ordinary radio apparatus can be utilised, standard variable condensers of normal design are available, and small quantities of material suffice for a measurement.

In measuring the dielectric constant, the problem in the case of a liquid or solid is to measure the electrical capacity of a condenser filled first with air and then with the liquid or solid under investigation. For gases and vapours it is necessary to be able to evacuate completely the condenser so as to measure the capacity *in vacuo.* The cell capacity commonly used is about $100\mu\mu$ F for gases and vapours, and rather less for solids and liquids. Two types of apparatus are widely used for measurements at radio frequencies. In one a valve oscillator of fixed frequency excites a tuned circuit included in which is the condenser containing the substance under investigation. The voltage developed across this circuit is measured with a valve voltmeter and is a maximum at resonance. The point of resonance having been accurately determined for the empty cell, the medium is introduced at any desired concentration and resonance again obtained by compensating for the change of capacity with a standard variable condenser. A method of this type has been successfully used by Groves and Sugden (J.C.S. 1934, 1094) for vapours. The second method employs two high frequency oscillators which are loosely coupled so that an audible beat note is produced. The condenser containing the substance is included in one of the oscillatory circuits, and changes of capacity are compensated by a standard variable condenser, the beat note always being adjusted to the same value. In some cases it is sufficient to tune to the "silent point" at which both oscillators are in tune and there is no beat note. More accurately, the beat note can be adjusted to be in tune with an electrically maintained tuning fork, or can be compared with a fixed audio frequency by means of a cathode ray oscillograph. In this latter case when the beat frequency bears some simple relation to the fixed frequency, conveniently obtained from a small oscillator, a characteristic Lissajous figure is obtained.

The dielectric constant is only slightly greater than unity for gases and vapours under normal conditions, is between 2 and 10 for the majority of liquids and solids, but may rise much higher, *e.g.* 80 in the case of water. According to Maxwell the dielectric constant should be equal to the square of the refractive index, measured at the same frequency, and in many cases this is found to be approximately true, even when the refractive index for visible light is used. In other cases the relation breaks down completely when the frequency is not the same for both measurements.

Dielectric constants are of importance in connection with the measurement of dipole moments. Any polar molecule, that is one in which the mean electrical centres of the positive and negative charges do not coincide, will have a dipole moment, μ, determined by the magnitude of the equal positive and negative charges multiplied by the distance between them. Such a molecule will tend to orient itself in an electric field but will have to contend with thermal agitation, the disturbing effect of which increases with rising temperature according to the relation deduced by Debye. The Debye equation can be written in the form

$$\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{d}=a+\frac{b}{T}\mu^2, \quad . \quad . \quad . \quad (1)$$

where M is the molecular weight of the substance under consideration, d its density, T the

absolute temperature, a a constant for any given substance, and b a constant for all substances. It is possible to obtain the dipole moment from this equation by a series of measurements made at different temperatures, and this procedure is invariably adopted for gases and vapours. In the case of solutions, for which the experimental difficulties are much less, equation (1) is assumed to hold for dilute solutions in non polar solvents, and measurements are made over a range of concentrations so that the value for infinite dilution can be obtained. The dipole moment is calculated for a single temperature as the variation with temperature of the dielectric constant of a solution is not easily measured. The influence of solvent is, however, unfortunately not entirely eliminated by extrapolation to infinite dilution, and the results with vapours, although relatively few in number, seem definitely to be preferred. Values obtained for substances in the vapour state and in solution generally agree within 10%. A study of dipole moments leads to interesting conclusions with regard to molecular structure, and in many cases for molecules containing several polar groups it is possible to calculate the total dipole moment for each molecule by adding vectorially the various group moments. A full account of recent work on dipole moments is given by Glasstone "Recent Advances in Physical Chemistry," London, 1936.

A practical application of dielectric constants which is being developed is the determination of moisture in substances such as tea, grain, flour, cigarettes and tobacco by measurement of the dielectric constant of a known weight of the material in a suitably devised condenser. Since the basic material of the substances mentioned has a dielectric constant of the order of 5 while the value for water is about 80, it is apparent that the dielectric constant will be sensitive to small changes in the moisture content and comparatively insensitive to changes in the basic material. Any of the ordinary types of dielectric constant apparatus already mentioned can be adapted for this purpose; also commercial apparatus is available (Cambridge *Instrument Co*). Some trouble may be experienced by reason of the large power loss involved with the materials mentioned, especially when very moist. If the damp material forms the dielectric of the tuning condenser of an oscillator, the output will be much reduced, and similarly if present in the condenser of a tuned receiving circuit, the resonance curve will be flattened. These effects are minimised by making the cell capacity small and arranging it to be only a fraction of the total capacity. Moisture content up to and above 20% can be measured, the relation between dielectric constant and moisture being approximately linear. It is important to calibrate the apparatus with material similar to that for which the method is required, the moisture for this purpose being determined by oven drying or other convenient means. A. E. M.

Polarographic Analysis.—Automatically recorded current-voltage curves for a dropping mercury electrode may be employed for the quantitative and qualitative analysis of an aqueous or alcoholic solution containing metallic ions or reducible material either inorganic or organic. An apparatus for this purpose has been devised by J. Heyrovský and M. Shikata (Rec. trav. chim. 1925, 44, 496). The liquid to be analysed forms the electrolyte in a cell A (*see* Fig. 1) of which the anode is a pool of mercury and the cathode a glass capillary tube of 0·01–0·03 mm. diameter from which mercury drops at the rate of 1 drop in 1–4 seconds. The potential across the cell is slowly increased by means of a rotating potentiometer B which is directly geared to the recording drum C around which is wrapped a piece of photographic paper. The current flowing through the cell is recorded on the drum by a spot of light reflected from the mirror of the galvanometer D which is connected in series with the cell by way of the variable shunt resistance E. This shunt enables the sensitivity of the arrangement to be varied as necessary.

No current is passed by the cell until the

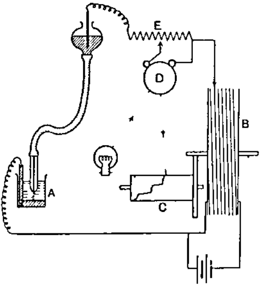

FIG. 1.

deposition or reduction potential of one of the substances present in solution is reached. A sharp increase in current then results and concentration polarisation sets in; that is, the mercury-water interface becomes denuded of reducible material by electrolysis and further electrolysis is limited by the rate at which fresh material diffuses to the interface from the main bulk of the solution. Further increase of the voltage results in no further increase in current until the next deposition potential is reached, when the phenomenon is repeated. In this way a curve consisting of a series of steps is obtained; the voltage at which a step occurs indicates qualitatively the substance responsible and the height of the step its concentration.

Determinations may be made in faintly acid ($p_H \nless 3·5$), neutral or alkaline solutions. With the exception of Mg all the common cations may be detected and determined in this way. Where two or more substances with the same or but slightly different deposition potentials are present together, separation may be achieved

by the addition of a complex-forming reagent such as potassium cyanide or ammonium oxalate. The resulting complex ions frequently have deposition potentials different from one another and from those of the free ions.

Among reducible substances determinable by this method are chromates, iodates, bromates, nitrates, dissolved O_2, H_2O_2, dissolved NO, dissolved SO_2, organic nitro-compounds, ketones, aldehydes, azo-compounds, etc.

Numerous other analytical applications have been described by J. Heyrovský and others (for example, Coll. Czech. Chem. Comm. 1929, **1**, 19, 387, 429, 477 ; *ibid.* 1930, **2**, 134, 489 ; *ibid.* 1931, **3**, 233, 354, 396, 406, 418 ; Rec. trav. chim. 1925, **44**, 514, 520, 528, 850 ; Mikrochem. 1932, **12**, 25). H. C. G.

Azeotropes : Their Analysis and Use in the Identification of Volatile Organic Liquids.—When the vapour pressures of certain mixtures of liquids are plotted against composition the curves show at particular concentrations a maximum or a minimum value of the vapour pressure, corresponding respectively with a minimum or a maximum boiling-point. To these mixtures the term "azeotropic" has been applied (Wade and Merriman, J.C.S. 1911, **99**, 1004). If a mixture has a minimum boiling-point it is said to exhibit positive azeotropism, or azeotropism of the first kind ; negative azeotropism, of the second kind, is associated with a maximum boiling-point. Among azeotropic mixtures those of the first kind are predominant.

The existence of azeotropic mixtures presents to the analyst both the problem of separating the constituents and a means of identifying organic liquids. Chemical methods of analysis may be used if one of the constituents is an acid, a base, contains halogen, sulphur, etc., but in general physical methods are preferable. The solubility of one constituent in a third liquid may be employed, whilst if the qualitative composition of a binary mixture is known its quantitative composition may be arrived at by determining the density, index of refraction, optical absorption, electrical conductivity, viscosity, or some other property, and comparing the value obtained with those for a series of prepared mixtures of known composition.

In addition, the following distillation methods have wide applicability.

(1) To the binary azeotrope a third substance is added which forms a tertiary azeotrope with the other two. Since the ratio between the weight of the two constituents in the binary mixture differs from their ratio in the tertiary, then if the tertiary mixture has a boiling-point sufficiently lower than that of the original mixture a separation can be made (Young, J.S.C.I. 1900, **19**, 1072). For example, the distillation of wet ethyl alcohol to which benzene has been added gives a first fraction at 64·86° of the tertiary azeotrope H_2O–$EtOH$–C_6H_6; at 68·24° if sufficient benzene has been added a mixture of $EtOH$ and C_6H_6 distils, and finally at 78·3° pure alcohol alone. In practice this particular example is wasteful, but the method can be applied to the dehydration of other alcohols (*e.g.* *iso*propyl, *ter*-butyl, allyl).

(2) A third substance is added which forms another binary azeotrope with one of the constituents, the boiling-point of which is lower than that of the original azeotrope. On distillation the new azeotrope first comes off leaving behind the other constituent.

(3) The following empirical relationship deduced by Young and Fortey (J.C.S. 1902, **81**, 717, 739; 1903, **83**, 45) is applicable to many cases. For a positive azeotrope the ratio of the weight of the constituent not in excess in the original mixture and the weight of the distillate below the mid-point (*i.e.*, the temperature midway between the boiling-points of the constituents) is equal to the proportion of that constituent in the binary mixture. For negative azeotropes the ratio between the weight of the constituent not in excess and the weight of the residue at mid-point is equal to the proportion in the original mixture. Thus, knowing the proportion of the constituents in the azeotropic mixture, the composition of the original mixture may be determined. This method is also applicable to non-miscible and partially miscible mixtures, but it is unsuited to systems in which the azeotropic temperature is near to the boiling-point of one constituent, if that constituent is in excess.

(4) The variation in composition of the azeotrope with pressure (*e.g.* Swientoslawski and Karpinski, Compt. rend. 1934, **198**, 2166) may be used as the basis of an analytical method. For example, the azeotrope, $EtOH$–C_6H_6, boiling under reduced pressure, at 0°C. contains 4·5% $EtOH$; at 100°C. it contains 45% $EtOH$ (Rabcewicz-Zubkowski, Rocz. Chem. 1933, **13**, 193, 334).

Data essential for the working of the first three methods are to be found in the extensive tables of azeotropes given in the literature, notably in Maurice Lecat's "L'Azeotropisme," Lamartin, 1918, Bruxelles and in his subsequent publications (*e.g.* Z. physical. Chem. 1930, **146**, 232; Bull. Acad. roy. Belg. 1929, [v], **15**, 1073; Ann. Soc. Sci. Bruxelles, 1929, **49**, 261; 1930, **50**, 18).

The formation of azeotropes may be utilised for the identification of unknown volatile organic liquids, preferably in the pure state, although the presence of minor impurities does not seriously interfere. The method is limited to substances which boil without decomposition at atmospheric pressure and consists in measuring the difference in temperature between the boiling-point of one of a series of standard liquids and that of the binary azeotrope formed by the standard and the unknown liquid. Lecat's publications give constants for a series of the most suitable standard liquids which may be added to the unknown liquid boiling between 80° and 225°C., together with the degree of azeotropism which may be expected with different types of unknown compounds. In some cases two or three binary mixtures may have to be examined before the unknown can be completely identified. 5–20 g. of the unknown are required and the maximum time needed for examination is 4–5 hours.

H. C. G. and H. K. W.